COLLOIDS

COLLOIDS

A TEXTBOOK

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PREFACE TO SECOND EDITION

The general plan of this second edition is the same as that of the first, published in 1927. Newer investigations carried out since 1925 have considerably modified the author's ideas on several points and this changed point of view has been expressed in the present volume. A welcome opportunity was also afforded to correct a number of errors pointed out by interested readers and to add some material the inclusion of which was deemed advisable by the author himself.

A thorough revision has been made of the discussions dealing with the electric double layer. Unfortunately, Helmholtz's original concept is, at present entirely inadequate; hence the distinction between charge and ζ potential has been introduced very early and the diffuse double layer is discussed in greater detail. A recent paper by Freundlich c.s. which appeared in Z. physik. Chem. 141, 249 (1929) led the author to consider a radical change in the treatment of suspensoids. Although the attempt was finally abandoned as premature, the reader will notice the influence of Freundlich's article in several places.

Many alterations were made in the sections describing peptization, flocculation and its kinetics (H. Müller's researches) both for suspensoids and for emulsoids (coacervation), gelatinizing, emulsions and other topics. In order not to impair the usefulness of the book as a text, the increase in the number of pages has been kept within narrow bounds. For the same reason, the author gave up his original intention to enlarge Chapter II with important new developments (data of Harkins, Bartell, Adams and other investigators).

In conclusion it may be stated that the task of revision has been limited to bringing the text up to the level of 1929.

H. R. Kruyt

Van't Hoff Laboratory,
Utrecht, Holland
September, 1929

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EXTRACT FROM PREFACE TO FIRST EDITION

As is indicated on the title page, this book is intended for use as a textbook. In other words, it is the author's purpose to offer a main line of orientation to students who wish to become acquainted with the general trend of Colloid Chemistry or who desire to undertake research in this particular branch of Chemistry.

The limitations imposed by this purpose will be apparent in the general plan of the work and in the degree of completeness with which the subject is treated.

In the first place, the author, believing that the choice of a general plan of attack is a matter of personal preference, has deliberately chosen the methods of Physical Chemistry to outline the path along which the study of colloids should be pursued. On several occasions his personal opinion has been brought to the fore. This will be particularly noticeable in the treatment of lyophile colloids. It may be stated that in a textbook the subjective method of approach is not undesirable. In fact, it is of prime importance for a student to develop a trend of thought; whenever he is confronted with a definite line of reasoning, this trend will be an incentive either to adopt the new concept or to reject it; hence, a subjective treatment is conducive to independent study. As J. S. HALDANE has said, "the whole business of a university teacher is to induce people to think."

In the second place, a textbook cannot treat the subject matter exhaustively. Comprehensive works on Colloid Chemistry are, moreover, available, and it would be wholly superfluous to try to improve on an excellent volume like FREUNDLICH'S "*Kapillarchemie.*" The reason for the existence of a textbook lies in its limitation. This is true not only with respect to the number of subjects dealt with, but also with respect to the treatment of each separate subject. Completeness has nowhere been the aim, but the arguments are constantly advanced.

VAN'T HOFF LABORATORY,
Utrecht,
Spring, 1926.

PUBLISHER'S NOTE

To Professor van Klooster, of the Rensselaer Polytechnic Institute, Troy, N. Y., who has translated the Dutch manuscript, the author is indebted for his painstaking labor in rendering the text in English and for the most valuable criticisms which he has offered.

One cut has been borrowed, with the permission of the publishers, from Dr. Getman's "Outlines of Theoretical Chemistry," and one from Dr. Holmes' "Manual of Colloid Chemistry."

Acknowledgment is also due the firm of Carl Zeiss, in Jena, for the use of the electroplates for Figs. 65, 67, 69, and 70.

CONTENTS

PAGE

Preface to Second Edition v

Extract from Preface to First Edition vii

PART I: GENERAL INTRODUCTION

CHAPTER

I. Preliminary Consideration of Colloidal Systems . . 3

1. Colloidal Systems: Dispersion. 2. Electrical Properties. 3. Two Types of Colloids. 4. General Problems of Colloid Chemistry.

II. Boundary Phenomena 13

5. The Liquid-Vapor Boundary. 6. Mixtures, 7. The Liquid-Liquid Boundary. 8. The Solid-Gas Boundary. 9. The Liquid-Solid Boundary. 10. Adsorption of Electrolytes. 11. Theory of Langmuir-Harkins.

III. Capillary Electrical Phenomena 51

12. The Capillary Electrode. 13. Capillary Electrical Processes. 14. Electro-endosmosis. 15. Flow Potentials. 16. Cataphoresis. 17. Migration Potential (Dorn effect). 18. Charge and Potential.

PART II: SUSPENSOIDS

IV. Stability of Suspensoids 67

19. Charge and Stability. 20. Electrolytes Carried down by the Flocculating Sol. 21. Flocculation Value and Concentration of Sol. 22. Heat Effect and Change in Volume at Flocculation. 23. Summary.

V. Charge and Stability 82

24. Electro-endosmosis and Charge. 25. Cataphoresis and Charge. 26. Flow Potential and Charge. 27. Measurements of Boundary Potentials. 28. Significance for Colloid Chemistry. 29. Summary. 30. Irregular Series. 31. Influence of Sols on Each Other.

VI. Constitution of the Double Layer 96

32. The Double Layer. 33. The Constituents of the Double Layer. 34. The Tin Oxide Sol. 35. Analogous Cases. 36. Extension of this Line of Thought. 37. Peptization. 38. Electro-valence of the Double Layer.

CHAPTER PAGE

VII. KINETICS OF FLOCCULATION 117

39. VON SMOLUCHOWSKI'S Theory of Flocculation. 40. Experiments on Rapid Coagulation. 41. MÜLLER'S Theory of Flocculation. 42. Experiments on Slow Coagulation. 43. Some Applications of the Preceding Trend of Thought.

VIII. OPTICAL PROPERTIES OF SUSPENSOIDS 129

44. TYNDALL Phenomenon. 45. Color of Suspensoids. 46. Behavior Toward X-rays. 47. Ultramicroscopy. 48. Determination of the Particle Size. 49. Double-refracting Sols.

IX. PROPERTIES OF SUSPENSOIDS FROM THE KINETIC POINT OF VIEW . 147

50. Brownian Movement. 51. Diffusion. 52. Osmosis. 53. Dialysis. 54. Ultrafiltration.

X. FORMATION OF SUSPENSOID SOLS 161

55. General Classification. 56. Condensation Methods. 57. Dispersion Methods.

XI. HISTORICAL OUTLINE OF THE DEVELOPMENT OF THE THEORY OF SUSPENSOIDS 169

58. Introduction. 59. The Nineteenth Century. 60. The First Decade of the Twentieth Century. 61. Latest Developments.

PART III: EMULSOIDS

XII. GENERAL PROPERTIES OF EMULSOIDS 179

62. Introduction. 63. Viscosity. 64. Electro-viscous Effect. 65. Cataphoretic Phenomena. 66. Size of Emulsoid Particles.

XIII. STABILITY OF EMULSOIDS 190

67. General Characteristics. 68. The Two Stability Factors. 69. Salting Out. 70. Dehydration by Tannins. 71. Summary. 72. Coacervation.

XIV. PROTEIN SOLS 205

73. Amino-acids in True Solution. 74. Colloid Character of Protein Sols. 75. Sols of the Casein Type. 76. Conclusions. 77. Special Properties of the Gelatin Sol.

XV. OSMOTIC PHENOMENA 219

78. Osmotic Phenomena of Colloids. 79. Theory of DONNAN. 80. Application to Colloids. 81. Measurements. 82. Membrane Potentials. 83. Abnormal Osmosis.

CHAPTER PAGE
XVI. GELS 229
84. Gelatinizing. 85. Thixotropy. 86. Classification of Gels. 87. The Silica Gel. 88. The Gelatin Gel. 89. Swelling. 90. Syneresis. 91. Optical Properties of Gels.

PART IV: SPECIAL CASES

XVII. SPECIAL SOLS 257
92. Cases Intermediate between Suspensoids and Emulsoids. 93. Soaps. 94. Emulsions. 95. Flocculation by Several Electrolytes. 96. Photo-colloid Chemistry.

AUTHOR INDEX 277

SUBJECT INDEX 283

PART I

General Introduction

COLLOIDS

CHAPTER I

PRELIMINARY CONSIDERATION OF COLLOIDAL SYSTEMS

1. Colloidal systems.—Dispersion. As a result of theoretical considerations which originated during the years 1880–90 we have at present a clear idea of dilute solutions such as those of glucose and barium chloride. The work of VAN'T HOFF, RAOULT, and others, dealing with the measurement of osmotic phenomena, viz., osmotic pressure, lowering of the freezing point, elevation of the boiling point, etc., enables us to find the molecular weights of dissolved substances, while, on the other hand, the researches of HITTORF, KOHLRAUSCH, ARRHENIUS and WI. OSTWALD, and in recent year the theories of DEBYE and HÜCKEL, have led to a knowledge of the formation of ions in solutions. We cannot grasp concepts developed by the above investigators unless we assume that the dissolved substance is split up into molecules or ions. The measurement of the quantities just mentioned is a measure of the chemical molecular weight and allows us to discriminate between conditions of dissociation and association that may exist for any given solute in any given solvent.

By using another nomenclature, the meaning of which is self-explanatory, we might say that glucose is *molecularly dispersed* in the solvent, while barium chloride is *ionically dispersed* and partly *molecularly dispersed* insofar as the undissociated molecules are concerned.

Whether the dissolved molecules and ions are present as such in the solution or combine with a number of solvent molecules (*hydration* or *solvation*) is a question that has been much discussed. Up to the present time it has not been answered satisfactorily although there are numerous indications in favor of a possible solvation.

It is a striking fact that an aqueous solution of glucose or of barium chloride is formed at once when either of these substances is placed in water and stirred for a few moments. The state of molecular dispersion is produced spontaneously; hence the free energy of the system water + dry substance is greater than that of the molecularly dispersed system.

Comparing the so-called *colloidal* solutions with the two mentioned above, we can make the following observations: If hydrogen sulphide is passed into a solution of arsenic trioxide, the latter will assume a yellow color and the solution will be found to contain an *apparently* homogeneous subdivision of arsenic trisulphide particles, which will be discussed later. If, however, finely powdered orpiment is placed in water, no arsenic sulphide will go into solution, even after several hours of stirring; it is evident, therefore, that the free energy of the system solid arsenic trisulphide + water is less than that of a homogeneous system.

The same statement holds for the behavior of a substance such as agar-agar. Agar-agar threads do not dissolve spontaneously in water, even at 50°. If, however, the temperature is raised to about 90°, there is formed an *apparently* homogeneous system which may be cooled to about 40° without any appreciable change in its stability. (At a still lower temperature there occurs a special process, *gel formation,* which for the present will not be further discussed.)

These two systems, therefore, are not formed spontaneously but can only be obtained in a roundabout way. Curiously enough, these colloidal systems do not show any osmotic phenomena. Their osmotic pressure, depression of the freezing point, and rise of the boiling point, if present at all, differ so little from zero that we are not certain whether they have any real meaning or not.

A comparison of the true solutions of glucose and barium chloride with the colloidal solutions of arsenic trisulphide and agar-agar leads to the assumption that the latter substances occur in colloidal solutions in a much coarser state of subdivision than the former ones, which, as stated before, must be molecularly dispersed. The comparison of these two kinds of solutions will be continued in the following paragraphs for the purpose of determining whether this supposition can be confirmed.

A substance that occurs in true solution can, of course, be precipitated, either completely or partially, by means of double decomposition with suitable reagents. If, for instance, phenylhydrazine is added to the solution of glucose, the dissolved substance is precipitated in the form of a hydrazone. If a solution of $MgSO_4$ is added to the solution of $BaCl_2$, $BaSO_4$ is precipitated. Stoichiometry teaches that in these cases there exists a simple ratio between the quantities of the reacting substances.

On adding magnesium sulphate to the colloidal solution of arsenic trisulphide, we find that minute quantities—about one millimole per liter—are sufficient to precipitate the arsenic sulphide, while, on the other hand, for an extremely small quantity of dissolved agar-agar, a concentration of about one mole of magnesium sulphate per liter is required. In neither case is there any stoichiometrical relation whatsoever between the reacting substances; hence we are dealing with a phenomenon quite different from the one in which molecularly dispersed substances are thrown out of solution by metathesis.

Assuming, then, that colloidal solutions are not molecular dispersions of the solute but consist of coarser aggregates, we naturally expect that the added magnesium sulphate molecules will react only with the *outer* molecules of the colloidal particles, and hence that simple stoichiometric relations will no longer exist between the added substance, which is split up into molecules (or ions), and the colloidal particles, which participate in the reaction with only a part of their molecules.

Several circumstances, therefore, justify our surmise that colloids differ from true solutions by their coarser subdivision. However, the realization of this fact was delayed for years by the circumstance that the microscope did not reveal any heterogeneity in colloidal solutions and that, furthermore, filter paper, even the finest, did not retain any trace of a residue in the filtration of colloidal solutions.

While colloidal solutions, when viewed under the microscope, are apparently homogeneous, to the naked eye they often appear to be turbid when examined *at right angles* to the path of a beam of light. When observed *in* the path of an incident beam they are perfectly clear. Since in the microscope we look *toward* the source of light, colloids appear transparent. A colloidal system, therefore, scatters the light sidewise, while a true solution, as a rule, does not. When the light that strikes the colloidal solution is partly reflected and partly transmitted, the liquid presents a turbid appearance.

The phenomenon of the scattering of light by colloidal solutions and nebulae is called the TYNDALL effect (see further Chapter VIII, Sec. 44). On this phenomenon is based the principle of the *ultramicroscope,* an optical instrument in which the TYNDALL light is observed microscopically. Experience has shown that this TYNDALL light is caused by the scattering of the light at the surface of the particles dispersed in the liquid. In the ultramicroscope, the light scattered by each particle may be observed separately, and we are thus able to recognize the presence of separate particles. The ultramicroscope confirms the conception developed above regarding the difference between true solutions and colloidal solutions. The discussion of the ultramicroscope and these optical phenomena will be deferred to Chapter VIII.

As to the passing of colloids through filters, mentioned previously, the following observation can be made. There is a characteristic difference between true and colloidal solutions: Substances in true solution normally pass through parchment paper, while colloids do not. GRAHAM observed this fact as early as 1861. At the same time he stated that while substances in true solution diffuse readily, substances in colloidal solution lack that property almost completely. As we shall find later (see p. 150), the very low rate of diffusion of substances in colloidal solution is closely connected with the fact that they are not as finely divided in the solvent as substances in true solution.

Researches with the ultramicroscope have shown that we can divide dissolved substances into three groups, depending on the state of subdivision: (1) particles that can be observed under the microscope are called *microns;* (2) particles that can be observed only by means of the ultramicroscope are called *ultramicrons* or *submicrons;* and (3) particles that remain invisible in the latter instrument are termed *amicrons.* The boundaries between these three groups cannot be sharply defined, since the visibility of a particle does not depend entirely on its size. As a first approximation, we may say, however, that the limit of microscopic visibility lies at 0.2μ, while the limit of ultramicroscopic visibility lies around $10 \mathrm{m}\mu$ [$1 \text{ mm.} = 1000\mu$; $1\mu = 1000 \mathrm{m}\mu$; $1 \mathrm{m}\mu = 10 \text{ÅU}$ (Ångström units)].

All such particles appear to be in a state of vigorous motion. This so-called Brownian movement (see p. 147) is closely connected with the kinetic energy of the molecules.

To summarize the previous discussion, it may be said that in true solutions matter is split up into molecules, while in colloidal solutions larger particles, polymolecular particles, are present.

It is customary to call a colloidal solution a *sol*, while the name *gel* is used exclusively for the jelly-like mass that is formed, when, for instance, a gelatin solution solidifies completely without any visible separation. This is called *gelatinizing*. The term *flocculation* is used for the process of precipitating the dispersed substance whereby the *dispersed phase* is separated from the *dispersion medium* (or *dispersing phase*). In some treatises, the name *gel* is also employed to designate a colloidal precipitate. This practice cannot be recommended.

True solutions and colloidal solutions differ morphologically in degree of dispersion. If mastic is dissolved in alcohol, a true solution is obtained. On pouring a little of this solution into water, we obtain a colloidal solution of mastic in water, as shown by the immediate appearance of the Tyndall effect. The water is called the *dispersion medium*, and the mastic the *dispersed* (or *disperse*) phase. English scientists speak of *internal* and *external phase*, while the French call the dispersed particles *micelles* or *granules* (reference will be made later to a difference between the meanings of these two words; *cf.* p. 109) and the dispersing phase *milieu extérieur* or *liquide intermicellaire*. The word *micell*(*e*) is also used considerably in English.

Heretofore, the dispersing phase has been tacitly assumed to be a liquid. There are disperse systems, however, that are built up differently. Wo. Ostwald has pointed out that, in general, disperse systems can be distinguished as follows:

1. $G + G$
2. $G + L$
3. $G + S$
4. $L + G$
5. $L + L$
6. $L + S$
7. $S + G$
8. $S + L$
9. $S + S$

In this classification, S represents the solid state (solidus), L the liquid state (liquidus), and G the gaseous state. Furthermore, the first capital letter indicates the dispersion medium, and the second the dispersed phase. System 1 is a mixture of two gases. Since gases mix freely and form molecular dispersions, the system $G + G$ falls outside the field of colloid chemistry. System 2 represents the condition known as a fog: liquid droplets dispersed in a gas such as air. System 3 is a smoke: solid particles dispersed in air. System 4 is a foam, consisting of isolated gas spaces enclosed in cohering liquid films. System 5 is the emulsion of one liquid dispersed in another liquid. System 6 is a suspension.

System 7 is a comparatively rare one. It includes the finely divided gaseous inclusions found in certain minerals. The gels, consisting of liquid enclosed in solid walls, belong to system 8. System 9 is represented by materials such as gold (or ruby) glass in which minute gold particles are dispersed in a solid mass of glass.

Although it is formally correct to consider all these disperse systems as more or less related to one another, the development of colloid chemistry has shown that only a few of them are closely connected, while others are but remotely related to one another. Colloid chemistry has been developed chiefly in the direction of systems 5 and 6, representing colloidal sols, and system 8, which is often formed from systems 5 and 6. It would be wrong, however, to suppose that the knowledge gained from these three systems might be transferred without change to systems 2 and 3, viz., to a fog or a smoke. Henceforth, the discussion will be confined to colloidal systems in a more restricted sense. A writer on dispersoid chemistry who attempts to discuss the general properties of *all* these systems is bound to fall into superficial generalities since the specific properties of the different systems show profound differences.

Nevertheless, it may be stated that disperse systems of widely differing character are possible and that the characteristics of a disperse system are not linked to any particular kind of substance. GRAHAM, therefore, was mistaken in his classification of colloidal and non-colloidal (or crystalloidal, as he called them) substances, since, in general, *any* substance can be brought into the colloidal state. Colloidality is not a specific property of a definite type of substance but represents a possible state, comparable with the liquid state, the gaseous state, and the solid state.

Moreover, crystallinity does not stand out in striking contrast to colloidality. The X-ray researches of DEBYE and SCHERRER (see p. 134) have shown that in the large majority of colloidal systems the dispersed particles are minute crystals.

2. Electrical Properties.—One of the most important properties of colloidal particles is the fact that they are generally electrically charged with respect to their surroundings. When an electric current is passed through a colloidal solution of As_2S_3, it will be found after a while that the dispersed substance has accumulated at the anode. Without claiming that anything else has occurred in the liquid but the displacement of the As_2S_3, one may state that the sulphide has migrated *as a whole,* whereas in a solution of copper chloride the chlorine moves toward the anode and the copper toward the cathode. (See however Sec. 38)

Furthermore, the direction in which a colloidal particle moves, with respect to the electric current is a specific property of that particle. An As_2S_3 particle moves toward the anode and is therefore, apparently, negatively charged, while a particle of Fe_2O_3 moves toward the cathode and must, therefore, be positively charged. A sol of ferric oxide may be prepared by hydrolyzing ferric chloride at higher temperatures. On pouring a few drops of a solution of this substance into boiling water, hydrolysis takes place and a reddish-brown iron oxide sol is formed. If the solution thus obtained be placed in a dialyzer (a vessel over the bottom of which parchment paper is stretched; see Fig. 1), the hydrochloric acid which is formed passes through the parchment into the outside water (which may be renewed repeatedly) while a pure colloidal solution of ferric oxide remains behind.

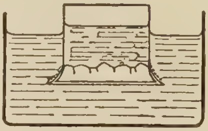

Fig. 1.

In subsequent chapters, it will become evident that there is an intimate connection between the electrical properties of a sol and added electrolytes. It has been known for a long time that many colloidal solutions are extremely sensitive to small quantities of added electrolytes. Linder and Picton have studied this relationship in detail. Although these matters will be fully discussed in Chapters IV and V, their results may be summarized here in the following statement: For a negatively charged colloid, the amount of electrolyte required to produce precipitation is, in general, determined by the valence of the cation of that electrolyte, the valence of the anion being of subordinate importance. For a positively charged sol, the valence of the anion determines the precipitating power of the electrolyte.

In general, a monovalent ion has a mild flocculating power; a divalent ion is much stronger in this respect; a trivalent one is still more powerful; and so on. In the case of the particular As_2S_3 sol used, the *coagulating point* (or *limiting value*), i.e., the concentration of electrolyte required to precipitate the sol completely in two hours, is 56 millimoles per liter for KCl, 0.68 millimole per liter for $BaCl_2$, and 0.091 millimole per liter for $AlCl_3$. Hence the flocculating powers of these electrolytes are in the ratio of 1 : 82 : 616. The converse of these relationships is presented by the previously mentioned positively charged Fe_2O_3 sol. Whereas 60 millimoles of KCl (monovalent anion) were required for precipitation, only 0.6 millimole of K_2SO_4 (divalent anion) produced the same effect.

3. Two Types of Colloids.—In the previous paragraphs it has been shown that colloidal systems have three general characteristics: (1) they are not optically void but show the TYNDALL effect; (2) when dialyzed they appear to contain particles that do not pass through parchment; and (3) they migrate under the influence of a difference in electric potential. Although all colloidal systems have all these properties in common, they fall, nevertheless, into two large classes. These two groups have been designated as *suspensoids* and *emulsoids*. In another classification, the terms *lyophobe* and *lyophile* are employed. On the correctness of these nomenclatures, an opinion will be expressed later (see p. 179). The differences between these two groups are as follows:

(*a*) The suspensoids, or lyophobe colloids, to which belong the metal sols, the hydroxide sols, and the sols of inorganic salts, are systems which in most of their physical properties differ only slightly from their dispersion media. The viscosity of a gold sol and that of an arsenic sulphide sol differ little from that of water. Emulsoids, or lyophile colloids, which include the sols of albumin and the higher carbohydrates, form disperse systems in which the properties of the dispersing phase are considerably modified by the dispersed colloid. The high viscosity of a glue solution is a familiar example.

(*b*) There is an important difference in the behavior toward electrolytes. Suspensoids undergo *flocculation* by the addition of minute concentrations of electrolytes, whereas large amounts of an electrolyte are necessary to precipitate emulsoids; the so-called *salting out* of proteins requires comparatively large concentrations of electrolyte (except in the case of salts of heavy metals). There is still another important difference in the precipitation of these two groups. Addition of water to the system after flocculation causes emulsoids to return to the state of colloidal dispersion, but does not have this effect upon suspensoids; hence, *flocculation* is as a rule, *irreversible*, for suspensoids, and *reversible* for emulsoids.

(*c*) The ultramicroscopic image of one group is often different from that of the other. Most suspensoids give a well-differentiated ultramicroscopic picture consisting of bright particles in vigorous Brownian movement. Emulsoids, however, usually show only a diffuse light cone.

(*d*) Finally, the electrical properties are quite different. A suspensoid, ordinarily, has an electric charge of a definite sign, and only by very special methods (to be discussed later) is it possible to change this sign. On the other hand, most emulsoids, more particularly protein sols, change their charge readily, so that they are positively charged in an acid medium and negatively charged in an alkaline medium.

From the first-mentioned difference it follows immediately that there is apparently no mutual relation between the suspensoidal particles and the dispersion medium. Hence, the properties of the latter hardly change, whereas in emulsoid systems, which are rightly called lyophile, a reciprocal action between the dispersed phase and its medium takes place. This explains the striking contrast in the behavior of the two classes of sols. Although the opposing characteristics are not absolute (no contrasts ever are, for that matter!) it is expedient to accept the above systematic distinction between these two main groups of colloids.

4. General Problems of Colloid Chemistry.—In the preceding sections it has been shown that colloidal systems are systems in which a substance, although not in true solution, is nevertheless present in a state of fine division. The question now arises: How is it possible for such a system to maintain itself? As we know, the boundary between each particle and the *dispersion medium* is the seat of an interfacial energy which always strives to unite the particles in order to reduce the interfacial area. This tendency of particles to unite and form larger aggregates is universally known: small droplets tend to unite and form drops; small crystals grow together and form large units.

Since the particles in a colloidal solution are in Brownian movement, they are continually in a condition to collide with each other. At first sight it is inconceivable why the boundary tension just referred to does not cause the particles to cling together whenever a collision occurs, and thus destroy the colloidal system. It is an equally striking fact, that, at least in the case of suspensoids, the addition of a small quantity of electrolyte brings about a condition which really is in agreement with this expectation: on the addition of an electrolyte the dispersed particles unite, the system exhibits flocculation, and the disperse system is destroyed.

Hence, the object of the present discussion is, (1) to explain the comparatively great stability of the colloidal solution, and (2) to show why and how electrolytes can destroy this stability.

The first step will be to give an account of what really does take place in the interfacial boundaries. Chapter II will be devoted to this problem.

Secondly, the large part played by electrolytes, in connection with the fact that most sols are electrically charged, gives rise to the assumption that special electrical causes have an important bearing on the phenomena under consideration; hence the electrical conditions in the interface between particle and medium must be closely examined in order to solve the problems just mentioned. Chapter III will deal with this interfacial electricity, while in Chapter IV the facts established in the two preceding chapters will be developed into a theory of stability which, at present applies only to suspensoids.

CHAPTER II

BOUNDARY PHENOMENA

5. The Liquid-Vapor Boundary.—The best-known boundary phenomenon is that which exists at the surface of a liquid in contact with saturated vapor or air. We are all familiar with the appearance of a concave or convex meniscus and with the rise and fall of liquids in capillary tubes.

Laplace, as early as 1806, evolved a theory to account for these phenomena, basing his reasoning upon the idea that liquid and vapor meet sharply in *one* plane. Later, van der Waals revised the theory of Laplace, working on the assumption that the transition from liquid to vapor is not discontinuous but continuous.

The condition of the molecules near the boundary is depicted in Fig. 2. The basic idea is that the molecules exert an attraction upon one another, in such a way that at a certain distance from a given molecule the attraction exerted upon it becomes negligible; hence each molecule is assumed to be surrounded by a sphere of attraction. If a molecule is within the sphere of attraction of another molecule, each exerts a noticeable attractive force upon the other. In Fig. 2 are sketched a number of molecules with their surrounding spheres of attraction. If the lower part of the figure represents the liquid and the upper part the vapor, it will be seen that a molecule within the liquid is usually so balanced that in the upper half of its sphere of attraction there are as many molecules as in the lower half. Such a molecule is considered to be attracted equally strongly in all directions. On approaching

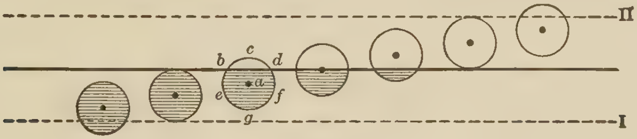

Fig. 2.

the boundary, we soon meet a particle, such as *a*, having a sphere of attraction in which the lower half is completely filled with molecules of liquid while the upper half is only partly filled. Since the vapor has a lower density than the liquid, there are fewer molecules in the segment *bcd* than in the equally large segment *efg*, and consequently the force tending to draw *a* upward is less than that tending to draw it downward. Such a molecule will be subjected to a one-sided attraction toward the liquid. It is clear that the same is true of all molecules between lines I and II. According to this mode of reasoning, each liquid is under a so-called internal pressure, as was indicated in the theory of Laplace.

It is evident, however, that the real relationships are not as they appear in the figure, where a sharp boundary surface (the fully drawn line) is assumed. Since the molecules situated between lines I and II are more strongly attracted toward the liquid, the closer they are to the boundary surface, it is evident that a state of equilibrium must be established, so that a density gradient between lines I and II exists. Hence, instead of a boundary *surface*, there is a boundary *layer*, which is not a mathematical plane but a layer of a certain thickness. For this reason, the expression "boundary layer" will henceforth be employed, rather than "boundary surface."

Extensive researches of van der Waals [1] and his pupils have made it clear that this continuous density gradient accounts for the so-called surface tension. The internal pressure is, as we have seen, a force acting in a direction *perpendicular* to the boundary surface; the surface tension, however, is a force acting in a direction *parallel* to the boundary surface and tending to decrease the surface to a minimum. Hence, an increase in surface requires the expenditure of energy, since it is a movement against the direction of the force. The surface is, therefore, the seat of a surface energy; and, if we define the surface *tension* as the force that operates in each square centimeter of cross section of the surface to hold it together, the surface *energy* must be the work necessary to increase the surface by one square centimeter (at constant temperature).

This line of reasoning was applied to the example of the liquid-vapor boundary, but nowhere was anything introduced that was specific for this combination. Precisely the same reasoning would apply if the lower half of Fig. 2 were assumed to represent, for instance, liquid phenol, and the upper half water (more correctly speaking, if the figure were assumed to represent the equilibrium between two liquid phases in the system water-phenol). Consequently the same phenomena occur at the boundary of two liquids, as will be discussed in Sec.7.

As an example of the effect of surface tension, it may be noted that small droplets tend to distill to larger ones. This can be readily observed under the microscope by placing a number of drops in a cell of a microculture slide. It is evident that small drops have a greater vapor pressure than large ones, since one gram of small drops has more potential energy than one gram of large drops. If both are to be vaporized, different amounts of energy will be required; hence these two kinds of drops cannot exist in equilibrium with the same vapor. (For a further discussion, see Sec. 87.)

Similarly, since small crystals sublime to large ones, we may conclude that there also exists a surface tension at the boundary of a solid in contact with its vapor. (See further, p. 26.)

The surface tension exerts, so to speak, a compressive force on a drop. The magnitude of this pressure can be easily computed. Let us consider a drop with radius r (Fig. 3) at the end of a capillary tube, connected on the other side with a large volume of liquid. The volume of the liquid can be changed by means of the piston Z. When the drop at the end of the capillary is in equilibrium with the large mass of liquid, the work done in slightly changing the position of the piston must be equal to the work required for a corresponding increase of the surface of the drop. Or:

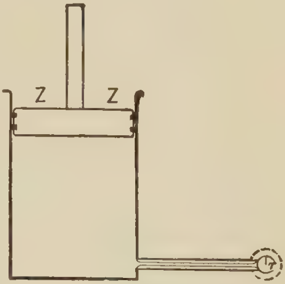

FIG. 3.

$$Pdv = \sigma d\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which P is the pressure exerted, dv the change in volume, σ the surface tension, and $d\omega$ the change in the surface area.

For a change in radius from r to $r + dr$, the increase in volume is $4\pi r^2 \times dr$, while the increase in area amounts to

$$4\pi(r + dr)^2 - 4\pi r^2$$

or

$$4\pi r^2 + 8\pi r dr + 4\pi dr^2 - 4\pi r^2,$$

which, neglecting dr^2 (a quantity of the second order), becomes $8\pi r dr$.

Hence, equation (1) is changed to:

$$P \times 4\pi r^2 dr = \sigma \times 8\pi r dr$$

or:

$$P = \frac{2\sigma}{r}.$$

It follows that the amount of compression resulting from surface tension becomes greater as the radius of the particle becomes smaller. It is, therefore, possible for the density of small particles to be somewhat greater than the density of the larger aggregates from which they were derived.

The surface tension (σ) can be determined by different methods. The first to be mentioned is that which makes use of the capillary rise (or fall), h. The relation between h and σ is given by the equation:

$$h = \frac{2\sigma}{d_L R g}.$$

in which d_L is the density of the liquid, R the radius of the capillary, and g the acceleration due to gravity. The angle of contact which the liquid makes with the walls of the tube is here assumed to be zero.[2, 12]

The surface tension is not always measured in absolute units. The alternative consists in establishing a comparison with water as a standard. This method, of course, can be applied also to the measurement of the capillary rise. Using the same capillary, we determine first the rise for water and then the rise for the liquid under observation. In this manner, we calculate the relative surface tension without measuring the diameter of the capillary.

Another method for the determination of surface tension is that which employs the *stalagmometer*.[3] This apparatus (Fig. 4) consists of a pipette, the end of which is ground flat (in order to give a larger dropping surface) and then polished. A constriction at the bottom of the tube causes a retardation in the flow of the liquid. The drops form at the flat tip, and fall as soon as the force of gravity balances the surface tension. The greater the latter the larger the size of the drops formed. For a given volume of liquid, the number of drops formed is inversely proportional to the surface tension. Using a definite volume, we first determine the drop-number for water, and then, with the same volume, the drop-number for the sample liquid. Or, we may proceed differently. Filling the pipette, first with water and then with another liquid, we may *weigh* a number of drops.[4] By means of the specific gravity of the liquid, the results are calculated in terms of equal volumes.

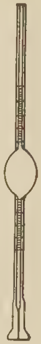

Fig. 4.

A third method is that of the so-called maximum bubble pressure.[5] The tip of a tube, through which air (or another gas) is blown, dips first into water and then into the sample liquid. The pressure required to let the gas-bubble escape from the tip is a measure of the surface tension.

A fourth method consists in measuring the force necessary to remove an object from the surface of the liquid. This force is measured with a balance.* As objects, a small plate, a ring,[6]

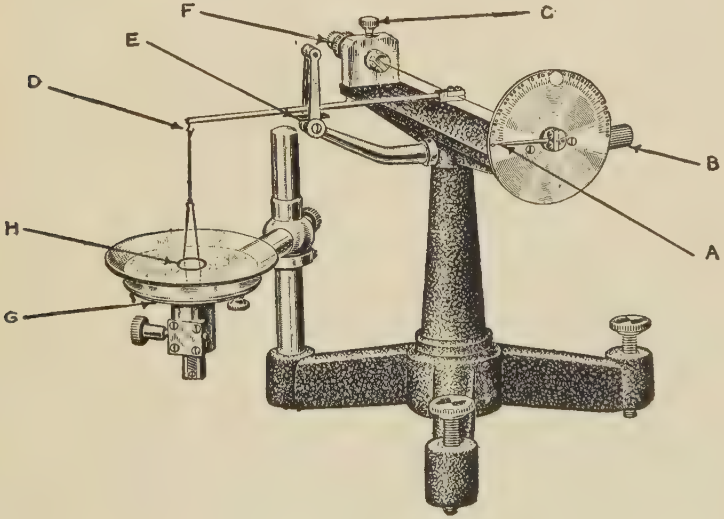

Fig. 5.

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* A very convenient instrument is the micro-torsion balance made by the Central Scientific Co. (Chicago, Ill.) (Fig. 5.)

or a rod[7] may be used. This method is especially well adapted for relative measurements, although it can also be used for absolute measurements.[7]

6. Mixtures.—We shall now consider the effect of added substances on the surface tension of a liquid, for instance, water. For the present, however, electrolytes in general are excluded, since these give rise to more complicated capillary electrical phenomena. (See p. 39.)

In studying the effect of added substances on the surface tension of a liquid, we find that this effect varies greatly for different substances. Some substances lower the surface tension; others leave it unchanged; while a few are capable of raising it. If there is a change, however, the effect always increases with the concentration.

Another important property, common to systems of more than one component, and known for a long time, is that the concentration in the interior of the liquid and that in the boundary layer are *not* always the same. In the boundary layer, the concentration of one of the components is often much greater than in the liquid itself; sometimes, however, it is smaller.

This phenomenon may be demonstrated by artificially increasing the surface of a liquid, e.g., by making it foam strongly, since a lamella of foam is a liquid which has an area large in comparison with its volume. Miss BENSON[8] has verified this fact by comparing the concentration in the foam obtained from an amyl alcohol solution with the concentration in the solution itself.

WILLARD GIBBS[9] first deduced thermodynamically the relation between the change of concentration in the boundary layer and the effect of the dissolved substance on the surface tension of the liquid. If a substance lowers the surface tension, the boundary layer is richer in this substance than the bulk of the liquid; and, conversely, if the substance raises the surface tension, the boundary layer is poorer.

Variations in the concentration in the boundary layer are commonly called *adsorption*. *Positive* adsorption is that which occurs when there is an increase in concentration; when a decrease in concentration in the boundary layer takes place, the adsorption is said to be *negative*.

The rule of GIBBS may be derived by considering the following isothermal cyclic process:

Imagine a liquid mixture with a surface tension σ and a surface ω, while the "osmotic pressure" in a volume v would be π.

(1) At constant volume, the surface is increased. This requires the work $\sigma d\omega$, while the osmotic pressure changes from π to $\pi + \left(\frac{\partial \pi}{\partial \omega}\right)_v d\omega$.

(2) The second step consists in keeping the surface constant while the volume is increased. In other words, the solution is diluted with the solvent while the shape of the container is changed in such a way that the total area remains constant. The work done is equal to the osmotic pressure times the volume change and amounts to

$$-\left\{\pi + \left(\frac{\partial \pi}{\partial \omega}\right)_v d\omega\right\} dv.$$

Owing to the dilution, the surface tension varies as a result of the change in concentration and becomes

$$\sigma + \left(\frac{\partial \sigma}{\partial v}\right)_\omega dv.$$

(3) Next, the original surface is restored and the system performs work equal to the surface tension times the change in surface, or

$$-\left\{\sigma + \left(\frac{\partial \sigma}{\partial v}\right)_\omega dv\right\} d\omega.$$

At the same time, the osmotic pressure reverts to the original value, π.

(4) Finally, in restoring the old volume, for which the work πdv has to be performed, the system is brought back to its original state. The sum total of the energy changes must be equal to 0:

$$\sigma d\omega - \left\{\pi + \left(\frac{\partial \pi}{\partial \omega}\right)_v d\omega\right\} dv - \left\{\sigma + \left(\frac{\partial \sigma}{\partial v}\right)_\omega dv\right\} d\omega + \pi dv = 0$$

Hence, the following relationship exists:

$$-\frac{d\sigma}{dv} = \frac{d\pi}{d\omega} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

From this equation of Gibbs, we can derive an expression for the excess concentration (positive or negative) in the boundary.

Let us assume that n moles are dissolved in v liters. If the substance is homogeneously distributed throughout the liquid, its concentration in the liquid is:

$$c = \frac{n}{v}$$

If we call the excess concentration in the boundary layer, per square centimeter, u, we obtain:

$$c = \frac{n - u\omega}{v} \quad \ldots\ldots\ldots \quad (3)$$

Equation (2) can be written:

$$-\frac{d\sigma}{dc}\cdot\frac{dc}{dv} = \frac{d\pi}{dc}\cdot\frac{dc}{d\omega} \quad \ldots\ldots\ldots \quad (4)$$

From equation (3), it follows that:

$$\frac{dc}{dv} = -\frac{n - u\omega}{v^2} = -\frac{c}{v}$$

and:

$$\frac{dc}{d\omega} = -\frac{u}{v}$$

Substituting these values in equation (4), we get:

$$-c\frac{d\sigma}{dc} = u\frac{d\pi}{dc}$$

or, since $\pi = RTc$, and $\frac{d\pi}{dc} = RT$, the final result is:

$$u = -\frac{c}{RT}\cdot\frac{d\sigma}{dc} \quad \ldots\ldots\ldots \quad (5)$$

From this equation, we see, in agreement with the rule of Gibbs, that u is positive, i.e., the boundary layer is richer in the dissolved substance when $\frac{d\sigma}{dc}$ is negative, or, in other words, when the surface tension decreases on addition of this substance. Conversely, the boundary layer is poorer in the added constituent when $\frac{d\sigma}{dc}$ is positive, i.e., when the surface tension increases with the concentration.

For the liquid-vapor boundary layer, it is extremely difficult to test this relation experimentally. In order to determine u, we must know the concentration of the boundary layer per square centimeter. It will be readily understood that it is exceedingly difficult to realize conditions under which the total surface of the boundary layer is known and, at the same time, the concentration of the boundary layer is accessible to determination apart from the remainder of the liquid. However, since the previous discussion does not include anything that is specific for the liquid or the vapor phase, equation (5) applies equally well to boundary phenomena between other phases. We shall presently see that verification of equation (5) is sometimes possible. (See Sec. 7.)

Positive adsorption is a much more important phenomenon than negative adsorption, for the following reason: By the addition of a second substance, u may be considerably increased but may not be greatly diminished. This becomes clear if we consider only the two extreme cases. Suppose we have a liquid of a certain concentration. Then the increase in the concentration of the boundary layer is, so to say, unlimited; hence, a very dilute solution can be extremely concentrated in the boundary layer. If, however, negative adsorption takes place, the concentration of the boundary layer can, in an extreme case, be equal to 0, but the boundary layer can never contain less dissolved matter than is present in pure water. While, for positive adsorption, the concentration can increase without limit, it can decrease only to a certain extent in the case of negative adsorption. Accordingly, we shall see that positive adsorption plays a more important rôle than negative.

This is still further emphasized by the fact that solutions in water are the ones most frequently discussed. Water, however, has an exceedingly high surface tension, as can be seen in Table I, where the surface tension (at 20°) is listed for a number of substances.

TABLE I

Surface Tension in Dynes per Centimeter at 20°

Substance	σ	Substance	σ
Ethyl ether	16	Carbon tetrachloride	26
Ethyl alcohol	22	Pyridine	38
Methyl alcohol	23	Benzene	29
Glycol	46	Water	73
Acetic acid	23	Bromine	38
Chloroform	26	Sulphur trioxide	30
Carbon bisulphide	33	Mercury	400

Only mercury, molten metals, and fused salts have surface tensions which exceed that of water. Added substances generally decrease the surface tension and therefore give rise to positive adsorption.

The influence which one substance exerts on the surface tension of another is primarily determined by its own surface tension. The curve representing the surface tension as a function of the concentration approaches a straight line as the surface tensions of the two constituents of the mixture approach equality. The additive, straight-line character of the curve disappears gradually with the increase in the difference between the surface tensions of the pure substances, and the curve may even exhibit a minimum (Fig. 6). If we consider the cases represented by the third and fourth curves in Fig. 6, we notice that the change in the surface tension with the concentration is greatest near the left-hand side of the diagram. Adsorption phenomena are therefore most pronounced for very small concentrations.

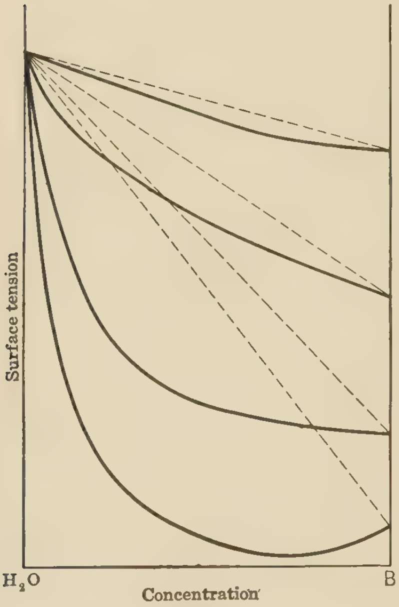

Fig. 6.

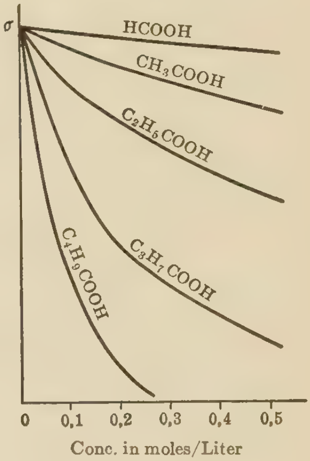

Fig. 7.

Organic substances, particularly those that have a long chain of carbon atoms or one or more benzene rings, exert the greatest *surface activity*, that is, they cause the greatest change in the surface tension of water. In general, the surface activity in an homologous series increases with the number of carbon atoms. An example is given in Fig. 7 where the surface tensions for aqueous solutions of fatty acids, from formic acid to valeric acid, are reproduced.

Looking at these phenomena from the standpoint of the theoretical physicist, we do not as yet possess a molecular theory which would enable us to predict a quantitative connection between surface tension and concentration. So far, it has only been possible to propose an empirical relation between these quantities.

Freundlich [10] has pointed out that the lowering of the surface tension by a dissolved substance, for moderate concentrations, can be represented by an equation of the following form:

$$\Delta\sigma = sc^{\frac{1}{n}}, \quad \ldots \ldots \ldots \quad (6)$$

where s and n are constants for a given substance. That the lowering of the surface tension is proportional to a fractional power of the concentration is indicated by the initial shape of the curves in Figs. 6 and 7. By the use of logarithms, the above expression may be written:

$$\log \Delta\sigma = \log s + \frac{1}{n} \log c. \quad \ldots \ldots \quad (7)$$

Log $\Delta\sigma$ and log c are in linear relation, which agrees well with the observations, as shown in Fig. 8, where the data of Fig. 7 are plotted logarithmically. From the fact that the lines in Fig. 8

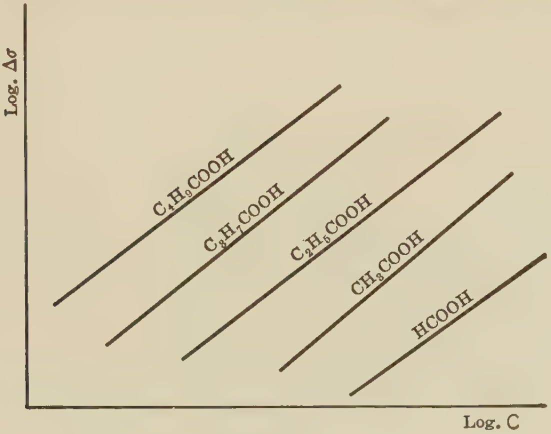

Fig. 8.

run parallel to each other, we note that $\frac{1}{n}$ for these different acids is practically constant.

We have seen in equation (5) that the amount of substance adsorbed is intimately connected with the change in surface tension. For a change of the latter proportional to $c^{\frac{1}{n}}$, the amount adsorbed will bear a similar relationship to the concentration.

Freundlich [11] has maintained, therefore, that for the amount x adsorbed at constant temperature the following relation exists:

$$\frac{x}{\Sigma\omega} = kc^{\frac{1}{n}},$$

where $\Sigma\omega$ is the total boundary surface. Hence $\frac{x}{\Sigma\omega}$ represents the amount adsorbed per square centimeter. This equation, usually called the adsorption isotherm, is poorly adapted to experimental verification in the gas-liquid equilibrium, for the same reasons that were suggested with regard to equation (5).

The speed with which a dissolved substance changes the surface tension of water is generally great. Within a few seconds, the surface tension reaches its final value. Since the process does not, however, take place instantaneously, we must distinguish between a dynamic and a static surface tension. The former is measured at a newly formed surface, whereas the second belongs to a surface that is completely in equilibrium with the interior of the liquid. Once in a while it happens, as for instance in the case of soap solutions, that the time required to establish equilibrium is quite considerable.

7. The Liquid-Liquid Boundary.—At the boundary between two immiscible liquids, there also exists an interfacial tension. This is evident at once from the fact that a small amount of oil introduced into water forms a round drop (flattened only by the force of gravity). We conclude that there is a tendency toward minimum surface; consequently, surface energy is present at the oil-water boundary. The conditions at the interface between oil and water are, in many respects, similar to those represented in Fig. 2. Also, the methods of measuring the interfacial tension can be carried out in a manner analogous to those discussed in Sec. 5. A capillary tube dipping below the interface of the two liquids enables us to measure the capillary rise or fall of the interface.[12] Using a stalagmometer filled with one liquid and dipping into the second, we can count the number of drops and arrive at a conclusion regarding the interfacial tension, just as in the case of liquid and air.[13] Even the method of "pulling apart" can be applied to the interface of two liquids.

If a foreign substance is dissolved in the water, the effect of the added constituent on the interfacial tension can be studied in the manner described above. For instance, the addition of a little soap decreases considerably the interfacial tension between oil and water.

In the case of the liquid-liquid combination, we are in a much more favorable position to test equation (5). For one reason, it is possible, as we have seen, to measure the effect of the substance to be adsorbed on the interfacial tension; moreover, we are able to divide one liquid into fine droplets of known dimensions and in this way create a large surface that is completely known. Lewis and Patrick,[14] in particular, have used this method to check equation (5), the former by measuring the adsorption of different substances by drops of paraffin oil (or of mercury) emulsified in water, the latter by doing the same for small droplets of mercury which moved in a stream through a liquid.

Patrick's work was carried out in an apparatus such as that sketched in Fig. 9. *A* is a reservoir containing mercury. By means of a ground-glass stopper, it is connected to a tube, *B*. Fine grooves in the stopper allow the mercury to fall in fine droplets into the tube *B*. The rain of mercury falls from *B* into the reservoir *C*, where it collects with the loss of its large surface.

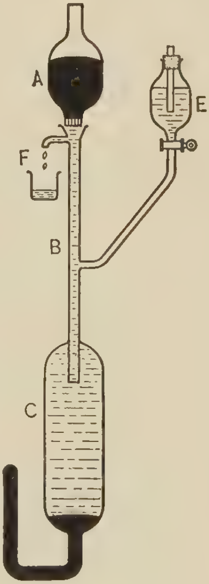

Fig. 9.

When *B* and *C* are filled, for instance, with a solution of picric acid in water, the adsorption of the picric acid by the mercury will lower the concentration in the tube *B*, while in *C* the adsorbed quantities will be released.

Since the rain of mercury exerts a strong stirring effect, it is necessary to keep the liquids in C and B from mixing.

A counter-current device from the reservoir E and the outlet F brings about a stationary condition in the upper part of the tube B and thus makes it possible to draw conclusions with regard to the change in concentration caused by the rain of mercury.

The results of LEWIS and of PATRICK approximately confirm the formula: the greater the quantity adsorbed, the greater the effect of the adsorbed substance on the lowering of the surface tension. For both phenomena, the order in PATRICK's experiments was the following: new fuchsin, picric acid, salicylic acid, mercurous sulphate. Quantitatively, the relation did not hold; the amounts adsorbed could not be calculated, by means of equation (5), from the lowering of the surface tension.

However, since we are dealing with electrolytes, the surface process is evidently complicated to a degree not covered by the assumptions underlying the formula of GIBBS. This deviation will be more fully discussed on page 39, where the influence of dissolved electrolytes will be dealt with.

8. The Solid-Gas Boundary.—It has already been pointed out (p. 15) that there must exist a boundary tension at the interface between solid substances. Unfortunately, there are no means at our disposal by which such boundary tensions can be measured. However, all phenomena thus far discussed that are related to boundary tension are plainly in evidence, and the relation between concentration and amount of substance adsorbed also applies here.

It is generally known that gases condense at the surface of charcoal, or, in other words, that gaseous adsorption takes place at the solid-gas boundary. A piece of charcoal, previously heated over a flame, on coming in contact with ammonia gas collected over mercury in a eudiometer tube, causes an immediate rise of the mercury column, due to the condensation of gas at the surface of the charcoal.

On page 24 the following relation was discussed:

$$\frac{x}{\Sigma\omega} = k \cdot c^{\frac{1}{n}}. \qquad \ldots\ldots\ldots \quad (8)$$

The total area $\Sigma\omega$ is a quantity which is not readily measured for a piece of charcoal. In order to check this equation, we start from the following consideration:

In all probability, the surface of 2 grams of charcoal will be twice that of 1 gram of charcoal, especially if the charcoal is so finely divided that it can be evenly mixed. Hence, we can replace $\Sigma\omega$ by m, where m represents the weight of the charcoal used. We must keep in mind, however, that the constants then only hold for one and the same sample of charcoal.

The formula of the adsorption isotherm then takes the following shape:

$$\frac{x}{m} = k \cdot c^{\frac{1}{n}}.$$

Since, for a gas that follows the law of Boyle, the pressure is proportional to the molecular concentration, we may write, instead of c, the gaseous pressure, P. Hence formula (8) becomes:

$$\frac{x}{m} = k \cdot P^{\frac{1}{n}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or, on changing to logarithms:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P.$$

This equation is expressed graphically by the curve drawn in Fig. 10. The adsorption is *relatively* greater the smaller the pressure.

In general, it may be stated that the results of numerous investigations are in agreement with this formula. Nevertheless, several attempts have been made to place the formula of the adsorption isotherm on a better theoretical foundation.

The first attempt to place the theory of adsorption on a kinetic basis was made by Langmuir.[15] The adsorbent is represented by a crystal lattice in the interior of which all valences are saturated, while at the surface this is not the case. Langmuir assumes that the unsaturated valences are responsible for the adsorption. These projecting valences are, however, distributed regularly over the surface and form adsorbing spaces in that surface. Gas molecules coming within the sphere of attraction of these spaces

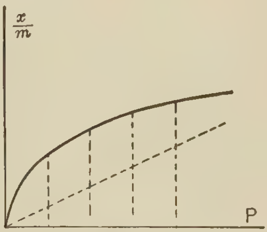

Fig. 10.

are adsorbed, but, owing to their kinetic energy, which acts in the opposite sense, they tend to escape; hence, we have, simultaneously, condensation on the surface and evaporation. A state of equilibrium is established as soon as the rate of condensation per square centimeter of surface is exactly counterbalanced by the rate of evaporation.

Let θ represent the fraction of the total number of available spaces occupied per square centimeter of surface; then $1 - \theta$ is the part that is unoccupied.

Furthermore, let α be the fraction of the total number of colliding molecules (μ) that adhere to the surface. When the gas is in equilibrium with the surface, the rate of evaporation must equal the rate of condensation, or:

$$\nu\theta = \alpha\mu(1 - \theta),$$

where ν is the rate at which the gas would evaporate if all available spaces were completely covered. From this equation it follows that:

$$\theta = \frac{\alpha\mu}{\nu + \alpha\mu}$$

On placing $\frac{\alpha}{\nu} = \beta$, we get:

$$\theta = \frac{\beta\mu}{1 + \beta\mu}$$

The number of molecules colliding per square centimeter (μ) is proportional to the gas pressure, P. For $\beta\mu$ we can write k_1P, by combining the proportionality factor and the factor β and calling the result k_1. Since θ is proportional to the number of adsorbed molecules, u, we can substitute u for θ and combine the new proportionality factor with k_1 in the numerator, thus obtaining another constant, k_2, whence:

$$u = \frac{k_2P}{1 + k_1P}$$

This equation gives us a relation between the amount of gas adsorbed, u, and the equilibrium pressure, P, resembling the relation expressed in Fig. 10. This becomes clear from a consideration of the two extreme cases. For very low pressures, k_1P in the denominator becomes negligible compared with unity, so that:

$$u = k_2P.$$

This corresponds to the initial steep slope of the adsorption isotherm, which starts almost as a straight line.

At very high pressures k_1P becomes very large compared with unity, so that:

$$u = \frac{k_2}{k_1} = \text{constant}.$$

This agrees with the practically horizontal portion of the adsorption isotherm at high pressures.

Langmuir has confirmed the accuracy of his formula in experiments with mica as adsorbent, using methane at pressures below 0.1 mm. mercury. The theory has been extended so as to include amorphous substances.

Although this line of reasoning is quite important for a clear understanding of adsorption phenomena, it nevertheless meets with some serious objections.

In the first place, we notice that adsorption is reduced to a process of chemical affinity, and yet it is not specific in character, being thus in striking contrast with the specific nature of chemical combination. The supporting evidence includes the fact that the chemically inert gases, helium and neon, are scarcely adsorbed by charcoal. It should be remembered, however, that argon is truly adsorbed.

Secondly, the theory is based on the idea that the adsorbed layer is only one molecule deep; otherwise a covered space would also be able to adsorb. Although the hypothesis holds true in certain cases (see p. 42) it is, as a general statement, open to grave doubt. For instance, de Boer[16] proved that iodine is adsorbed by calcium fluoride in a layer of polymolecular thickness.

Polanyi[17] has made a more complete study of the cases dealing with the adsorption of condensed gas or liquid, while Iliin[17] and several other workers have continued the investigations of kinetic phenomena begun by Langmuir. Since none of

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the theories advanced by these investigators covers the whole field of adsorption phenomena more accurately than FREUNDLICH'S classical formula, the use of this familiar expression will be continued in this book. The various theories relating to gas adsorption have been brought together in an interesting volume by HÜCKEL.[18]

The phenomena of gaseous adsorption show very clearly that the adsorption equilibrium is a reversible one. For instance, if we increase the volume after the adsorption equilibrium has been established, the carbon releases as much gas as is required by the above formula, in accordance with the change in pressure due to the increased volume.

FREUNDLICH, in his splendid book, "*Kapillarchemie*," has called attention to the following fact: When we perform adsorption experiments for a given adsorbent with a number of different gases, and then repeat these experiments with another adsorbent, we often find that in both cases the gases are adsorbed in the same order. This justifies to a certain extent the supposition that the specific character of an adsorption depends more on the properties of the gas than on those of the adsorbent.

A large surface, such as occurs in the case of amorphous carbon, cannot in itself be considered a sufficient reason for a great amount of adsorption; we frequently meet with large surfaces that adsorb only slightly. This is easily understood in view of the facts mentioned above. The adsorption process is determined not only by the surface capacity but also by the relation $\frac{d\sigma}{dc}$, that is, by the influence of the substance to be adsorbed on the boundary tension. The value of $\frac{d\sigma}{dc}$ naturally varies for different substances.

The solid-gas equilibrium can be readily measured, as far as the adsorption is concerned, since equilibrium conditions can be checked directly from the gas pressure and no analytical determinations of concentration have to be made. Various problems of general interest for the study of adsorption have, therefore, been carefully worked out for this equilibrium. One of these is the manner in which a mixture of two gases is adsorbed. Since this question will play an important rôle in a later part of this discussion, it may be stated here that in most cases *both* gases are adsorbed from a mixture of the two, but each is adsorbed to a lesser extent than if it were present alone. A certain mutual displacement exists, therefore, but in spite of this the completely reversible character of adsorption phenomena is maintained, the final equilibrium being independent of the order in which the gases are brought in contact with the adsorbent.

The speed with which equilibrium is established is, as a rule, quite considerable. A few minutes are more than sufficient to bring about a perfect adsorption equilibrium. If, however, any chemical reaction takes place subsequently, either between the gases and the adsorbent, or between the gases themselves in the adsorption layer, more time will be required to reach a final state of equilibrium.

9. The Liquid-Solid Boundary.—As evidence for the existence of a liquid-solid boundary tension, the facts mentioned at the beginning of Sec. 8 may again be cited. Here, too, there are indications that a boundary tension does exist. For instance, if a number of small crystals are in contact with their solution, while at the same time a few larger crystals are present, it is quite apparent that the smaller crystals are more soluble than the larger ones; hence the former dissolve continuously and the latter grow, since the solution is supersaturated with respect to the larger crystals. This phenomenon must likewise be explained on the supposition that a boundary energy plays a rôle just as with small drops which have a greater vapor pressure than large ones (see Sec. 87). This interfacial tension is as yet not accessible to measurement.

A number of adsorption phenomena which are of great importance in the study of colloid chemistry will now be discussed.

Adsorption experiments on a pure liquid in contact with a solid wall have not been made, and are naturally exceedingly difficult. The condition existing in the boundary layer of water in which carbon powder is suspended is, no doubt, different from that of pure water itself. A certain condensation of molecules, perhaps a displacement of the equilibrium between single and double molecules, takes place. This problem, however, has not been solved experimentally.

On the other hand, there have been frequent and successful attempts to determine the degree to which *a substance dissolved in water* is condensed in the boundary layer of a solid adsorbent. This problem is much easier to solve, since the amount adsorbed can be derived from the difference in concentration between the original solution and one with which the adsorbent is in equilibrium.

It has been known for a long time that the constituents of a solution can be removed by means of charcoal powder. Colored substances, in particular, are often removed in this manner. When charcoal is added to a solution of a dye, the intensity of the color will decrease or the color will disappear completely, depending on the amount of charcoal used. The same thing happens when a quantity of wool is employed. The adsorption of the color becomes manifest by the dyeing of the white adsorbent.

Regarding an adsorption process of this kind, a number of remarks may be made.

(*a*) This process is an equilibrium reaction and is quantitatively expressed by the equation of the adsorption isotherm, discussed in connection with equations (8) and (9), viz.:

$$\frac{x}{m} = k \cdot c^{\frac{1}{n}}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

where x is the total amount adsorbed, m is the amount of adsorbent used, and k and n are constants characteristic of the substance adsorbed.

By plotting the amounts adsorbed as ordinates against the equilibrium concentrations as abscissae, we obtain the curve represented in Fig. 11.

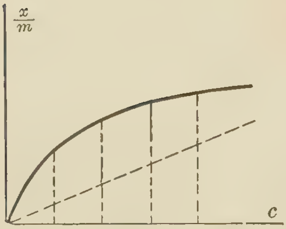

Fig. 11.

We have previously seen that the logarithm of the amount adsorbed must be proportional to the logarithm of the equilibrium concentration. In Fig. 12 a number of adsorption isotherms are reproduced, while in Fig. 13 the same isotherms are represented logarithmically. It will be noted that the lines are straight and more or less parallel to each other, which means that they have the same slope. Hence $\frac{1}{n}$ is a quantity of little specific character. In fact, its value lies mostly between 0.3 and 0.7. A like remark was made previously, on page 24, concerning the exponent in equation (6) indicating the relation between $\Delta\sigma$ and c.

It can readily be shown that this phenomenon is a true reversible equilibrium. This can be done by twice investigating the adsorption equilibrium of a solution in contact with an adsorbent: Starting from a certain amount of dissolved substance we measure the equilibrium concentration and then add a concentrated solution to the dilute system; next a concentrated system is diluted in such a manner that the same total concentration is reached as before. It will be seen that the equilibrium concentration for the adsorption process is the same in both cases.

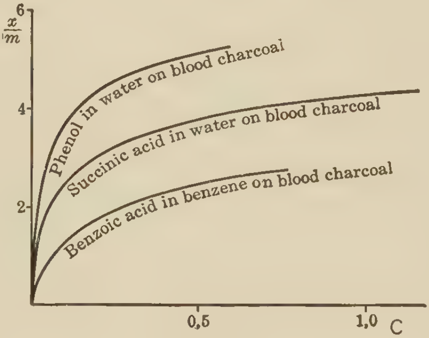

Fig. 12.

(*b*) The peculiar shape of the adsorption isotherm drawn in Fig. 11 shows that the effect of the adsorption is greatest in very dilute solutions. By comparing the amount adsorbed with the corresponding equilibrium concentration, we see that for small values of c this ratio is most favorable to the amount adsorbed. This inference is in complete agreement with the statement made on page 27.

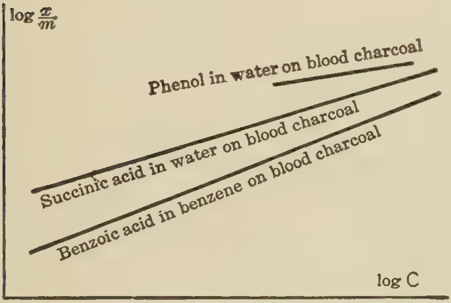

Fig. 13.

The fact that the adsorption process gives rise to such considerable displacements, particularly in very dilute solutions, can be used directly as a means of explaining numerous occurrences taking place in concentrations which, at first sight, appear incredibly small. Such are catalytic phenomena, enzyme reactions, and the effects of disinfectants and poisons. In all these processes, where extremely small concentrations have great effect, this action is due to the fact that somewhere an adsorption plays a rôle and a minute concentration is considerably increased in some boundary layer. It is perhaps not a mere coincidence that most of these substances are characterized by great surface activity.

Closely connected with this great activity in small concentrations is the fact that it is exceedingly difficult to wash out the last traces of an adsorbed substance. Washing is, in fact, nothing but following the adsorption isotherm in the opposite direction; by repeatedly pouring water over the adsorbent, we get equilibrium liquids of fairly high concentration, which are then removed. Owing to the peculiar shape of the adsorption isotherm, the effectiveness of washing decreases disproportionately as the amount retained by the adsorbent becomes smaller. Moreover, it is on these very properties that the fastness to washing of dyed textile fibers depends.

(*c*) These equilibria are likewise quite rapidly established. Robert Marc[19] has found that the adsorption of starch by powdered crystals is 90 per cent complete within a few seconds. In general, adsorption equilibria of this kind are established in a few minutes. Whenever we meet with an adsorption reaction that does not reach a final value within this period of time, we can be reasonably sure that it is not a simple one. For instance, in the adsorption of oxalic acid by charcoal, the condition reached after ten minutes apparently does not represent complete equilibrium since the concentration of the liquid continues to decrease, although very slowly, for several hours. Further investigations[20] have shown that the adsorbed oxalic acid reacts with dissolved oxygen, and that this process is catalytically accelerated in the adsorption layer. This combination of adsorption and chemical reaction occurs frequently. The fact that in the case of adsorption of dyes, such as fuchsine, by charcoal the establishment of a final equilibrium requires considerable time, must be ascribed to a chemical reaction (tautomeric change) in the solution.[21] Pure adsorption processes are characterized by a rapid attainment of the final state of equilibrium.

(*d*) Again, it may be stated that a large surface is in itself not sufficient to produce a high degree of adsorption, since the adsorptive power of an adsorbent depends specifically on the value of $\frac{d\sigma}{dc}$. Unfortunately, we cannot measure σ or its change with the concentration. Frequently the adsorbability is compared with the value of σ for the liquid-gas equilbrium, a comparison which is not directly permissible. Nevertheless, it so happens that substances that have great surface activity under one set of conditions are also well adsorbed under other conditions. For an homologous series this regularity holds, indeed, quite well; but whereas phenol lowers the surface tension of water less than amyl alcohol, the former is, nevertheless, better adsorbed.[22]

In general, the following rules can be given concerning the adsorbability of various substances:

The adsorption is *slight* for all inorganic substances with the exception of the halogens. Moreover, the salts of the heavy metals are adsorbed to a somewhat greater extent than those of the alkali metals. This is also true of all aliphatic substances having several hydroxyl groups, such as the sugars.

The adsorption is *stronger* for all other aliphatic substances and for the inorganic substances chlorine, bromine, and iodine.

The adsorption is *strongest*, generally speaking, for aromatic substances. The more benzene nuclei they contain, or the more complicated their structures are (as in the case of the alkaloids), the better they are adsorbed.

It may be stated in a general way that, apart from constitutive differences, a more complicated molecular structure coincides with greater adsorbability.

(*e*) As in the case of the solid-gas equilibrium, we find here that the order of adsorbability is the same for different adsorbents; but it should be repeated emphatically that only non-electrolytes are considered; the statement just made, viz., that the order of adsorbability is independent of the adsorbent, is not valid in those cases where phenomena of electro-adsorption predominate (see p. 39). The equality of the order of adsorption in various adsorbents is of considerable import, because in colloid-chemical discussions we often deal with adsorption processes that cannot be measured directly for colloidal particles. The corresponding adsorption experiments have usually been carried out by means of a suitable charcoal powder; hence, it is worth knowing that the order of these phenomena is the same in different adsorbents, and that some of the results may be transferred from one series to another.

(*f*) The influence of the temperature on the adsorption process is generally small. Ordinarily, the adsorption decreases with rising temperature. In Fig. 14 are reproduced the logarithmic adsorption isotherms for the adsorption, by charcoal, of acetic acid dissolved in water, at 0°, 50° and 94°. From the location of these lines it is seen that k decreases with rising temperature, while $\frac{1}{n}$ increases somewhat.

Sometimes we meet with cases in which higher temperatures are conducive to the adsorption process. In general, boundary tensions decrease with rising temperature; the liquid-gas boundary tension, as is well known, approaches zero; when the critical temperature is reached the boundary tension becomes zero. For the liquid-liquid interfacial tension this rule does not hold in all cases. The boundary tension, to be sure, approaches zero as the critical solution temperature is reached, and the rule is applicable to all systems having an *upper* critical solution temperature. But there are also systems that possess a *lower* critical solution temperature, and for these the boundary tension increases with the temperature. We do not as yet know what the conditions are for the boundary tensions at solid surfaces, but, knowing the behavior for liquids, we should not be surprised if the same two possibilities were found to occur at solid boundary surfaces.

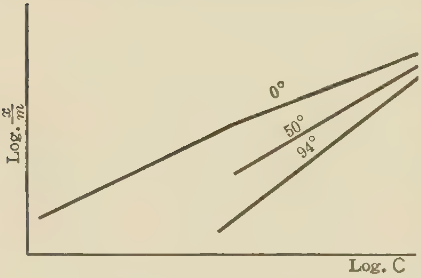

FIG. 14.

As stated above, the most frequent case is that in which the adsorption decreases at higher temperatures. According to the theorem of van't Hoff-Le Chatelier, we are dealing, in this case, with a process which takes place with evolution of heat. Hence the heat of adsorption is usually positive. It should be kept in mind, however, that this heat is a *differential* heat of adsorption for which there are at present no data available. Even determinations of *integral* heats of adsorption are quite rare. When 2 millimoles of crystal violet are adsorbed by charcoal from an aqueous solution of the dye, the heat evolution amounts to 16 calories.[23]

(*g*) The influence of the medium on the adsorption process may be embodied in the following rule: a substance that is easily adsorbed is a poor adsorption medium. The following example illustrates this clearly: Alcohol dissolved in water is fairly well adsorbed by carbon. A dye that is well adsorbed from its aqueous solution is poorly adsorbed from an alcoholic solution. Since alcohol itself is so well adsorbed, it is a poor adsorption medium.

This rule is easily explained when we remember that $\frac{d\sigma}{dc}$ is a measure of the adsorbability of a substance. In Figs. 15, *a*, *b*, and *c* are plotted the changes in the boundary tensions for the three systems just mentioned. Since alcohol is so well adsorbed, its $\sigma - c$ curve must have a steep slope. It was stated on page 21 that alcohol has a surface tension considerably below that of water (Fig. 15*b*). The same is true of the dye (Fig. 15*a*); but for the combination alcohol + dye (Fig. 15*c*) these boundary tensions necessarily differ very little. Hence the curve is only slightly inclined and the adsorption is small.

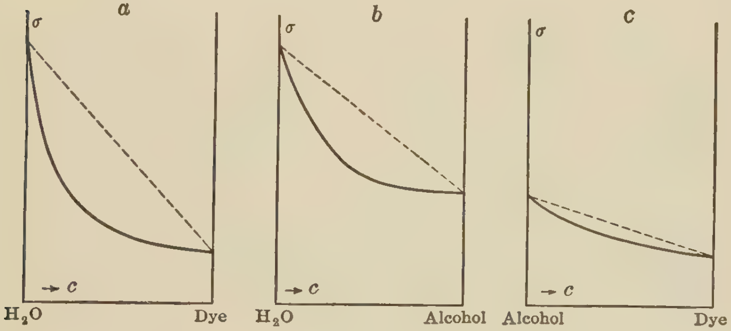

FIG. 15.

The foregoing statements indicate clearly that we can often successfully remove a substance, adsorbed in an aqueous solution, from the adsorbent, by pouring over it a liquid that is well adsorbed itself and hence is a poor adsorbing agent. This may possibly be connected with the fact that phenol dissolved in water is a strong disinfectant, while its action as such is much less when dissolved in oil or in alcohol.[24] At any rate, this fact corroborates the statement, made on page 33, that adsorption processes very probably play a rôle in disinfection.

More than one attempt has been made to determine whether the adsorption process is really a reversible equilibrium phenomenon, in other words, whether very small concentrations—mere traces,—removed by a clean surface from a solution, leave an equilibrium concentration in the liquid. The fact that a solution of a dye, on the addition of a sufficiently large amount of adsorbent, is completely decolorized might naturally cause one to ask whether there is not a complete exhaustion of the solution. Even so, it is quite possible, of course, that a few molecules are left in the solution, but that they are too few in number to be perceptible to the eye. From a kinetic standpoint, we must, however, assume that, for an adsorption surface in equilibrium with the liquid, as many molecules condense on each square centimeter of surface, per unit of time, as there are molecules going into solution. This necessitates the presence of a number of molecules in solution. Consequently, it is difficult to get away from the idea that a complete adsorption is an impossible limiting case. Although the peculiar shape of the adsorption isotherm shows that the attraction exerted on the dissolved molecules by a totally unsaturated surface can be very great, and that it approaches the limit, nevertheless the kinetic considerations just given seem to exclude an adsorption isotherm having a vertical tangent at the origin.

On the other hand, the question has been asked: Does the adsorption go on indefinitely with increasing concentration, or do we finally reach a state of saturation? In fact, there are indications that in some cases the adsorption isotherm runs horizontally at higher concentrations. Even so, the impression prevails that LANGMUIR'S idea of a monomolecular layer covering a surface is not generally valid.[16]

SCHMIDT [25] originally worked out a theory of adsorption based on the assumption of a saturation concentration, but later [26] he rejected this idea.

The phenomenon of the simultaneous adsorption of two substances has been very little studied for non-electrolytes. The impression prevails, however, that here too (see p. 30) both substances are adsorbed, each one to a lesser degree than if it were present alone, and in such a manner that the more strongly adsorbed of the two predominates in the mixture and thus hampers the adsorption of the second substance. We are, in these cases, dealing with phenomena of *displacement,* as is shown in the table below.[27]

TABLE II

Adsorption Displacement of Glucose by Various Urethanes

Initial solution: 9 g. of glucose per liter; 3 g. of blood charcoal.

Added urethane	Glucose		Urethane in moles per liter		
	c	$\frac{x}{m}$	Initial solution	c	$\frac{x}{m}$
None	5.3	1.23	—	—	—
Methyl	6.7	0.77	0.072	0.031	0.014
Ethyl	7.2	0.60	0.074	0.021	0.018
Propyl	8.3	0.23	0.070	0.009	0.020
Butyl	8.8*	0.07	0.070	0.004	0.022

* In the original article the value 7.8 is given, which is no doubt a typographical error.

This is a clear case of displacement. The adsorbed glucose is partly forced out of the boundary surface by the addition of a urethane. The more readily the added substance is adsorbed, the more pronounced is this displacement. The higher members of the homologous series are, as we know, always more strongly adsorbed than the lower. It is not necessary to discuss the significance of such phenomena for the elucidation of pharmacological processes.

10. Adsorption of Electrolytes.—An investigation of adsorption phenomena for electrolytes shows that their behavior is undoubtedly similar to that of non-electrolytes. For instance, we can readily determine the adsorption isotherm for a solution of oxalic acid, succinic acid, benzoic acid, etc. Nevertheless, it is apparent that influences of a different nature enter into play. This follows immediately from the fact that displacement phenomena as described in the previous section are only observed in case *both* adsorbed substances are non-electrolytes. On the other hand, an electrolyte is hardly affected by the presence of a non-electrolyte and, conversely, the adsorption of a non-electrolyte is not modified by an electrolyte.[28] If *two* electrolytes occur simultaneously, they generally *displace* each other, but in some cases both are adsorbed more strongly than when present alone.[29] Furthermore, an electrolyte is, as a rule, not adsorbed as a whole, on account of ionic interchanges between the ions of a substance already adsorbed and those of a newly adsorbed electrolyte.

The more complicated character of electrolyte adsorption is shown in an experiment which van Bemmelen[30] described as early as 1881. He prepared manganese peroxide from $KMnO_4$ and sulphuric acid. The acid was washed out until it could no longer be detected in the wash water. When a solution of KCl was added to the manganese peroxide, the solution showed an acid reaction. It seemed, therefore, that the KCl was hydrolyzed.

When a solution of new fuchsin in the form of its hydrochloric acid salt is adsorbed by blood charcoal,[31] the outside liquid becomes completely decolorized but appears to contain all the chlorine on the addition of HNO_3 and $AgNO_3$.

What happens in these two examples may be represented as follows: During the preparation of the manganese peroxide the latter adsorbs sulphuric acid in such a way that the SO_4 ions condense on the surface of the peroxide. Opposite each sulphate ion there are two corresponding hydrogen ions, so that a particle of peroxide is surrounded by an electric double layer, as sketched in Fig. 16. On the addition of a solution of KCl to the manganese peroxide powder thus prepared, an interchange occurs, the potassium taking the place of the hydrogen; the hydrogen enters into the solution in an amount equivalent to that of the chlorine present, and as a result the outside liquid gives an acid reaction. Apparently the same thing happens when new fuchsin hydrochloride is adsorbed. Here, too, a displacement adsorption takes place. However, it is less clear what the original ion is which is replaced by the ion of new fuchsin. It is probably derived from the ash content of the charcoal, since the phenomena, in the form described above, are different in case the charcoal is entirely free from electrolytes. Miller, for instance, found that ash-free, active sugar charcoal when placed in a salt solution adsorbs acid, the salt being hydrolyzed.[32]

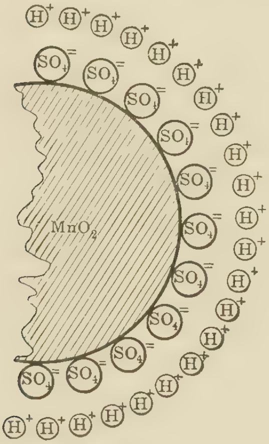

Fig. 16.

The adsorption of electrolytes, as sketched in these two cases, therefore, has not the one-sided character of the adsorption phenomena discussed previously. The latter were related to the lowering of the surface tension, while here a displacement adsorption occurs, electro-equivalent quantities being adsorbed and given off.[33] For this reason we may characterize these two different types of adsorption as *non-polar* and *polar* adsorption. It goes without saying that in the case of polar adsorption electrical phenomena play an important rôle, which will be fully discussed in the next chapter.

Since these two kinds of adsorption are quite different, the question might be raised whether it is reasonable to use the designation "adsorption" for both. By adsorption we mean, however, only an increase of concentration in the boundary layer irrespective of the mechanism by which this increase is brought about.

The adsorption of electrolytes often takes the character of a permutite interchange; hence, it is clear that this process is not affected by non-electrolytes, which cannot take part in it (MICHAELIS and RONA [33]). Before this fact was demonstrated, however, KRUYT and VAN DUIN [34] had already observed that phenol was not entirely without effect on the adsorption of KCl by blood charcoal. KOLTHOFF [35] has studied these matters, using ash-free sugar coal prepared according to the methods of BARTELL and MILLER,[36] and has found that this substance adsorbs electrolytes only slightly, since no interchange is possible. Insofar as they are adsorbed, however, displacement, for instance by alcohols, really does occur, as we are then dealing even when using electrolytes with non-polar adsorption. The slight adsorption of electrolytes in this case may be ascribed to their adsorption as molecules; hence it is equivalent to that of non-electrolytes and is subject to displacement by non-electrolytes.

11. Theory of Langmuir and Harkins.—Our insight into the condition of some substances in the adsorbed state, especially of those that are polar, has been considerably extended by the work of the aforenamed American investigators, who arrived, by different methods, and independently of each other, at the same conclusion, briefly formulated as follows: At an interface the molecules do not lie at random, but are oriented in a definite manner.

First of all, the researches of IRVING LANGMUIR [37] will be discussed: A very small quantity of oil, placed upon the surface of water, will spread over the surface. When the amount of oil is just sufficient to cover the surface, or is insufficient to do so, we may assume, on the basis of a theory advanced in 1899 by Lord Rayleigh,[38] that the oil layer is one molecule thick. Langmuir used this phenomenon as a starting point, and studied it in two ways.

Devaux [39] had previously performed experiments of the following nature: A glass tray contains water (Fig. 17*a*). Upon the surface of the water are placed two strips of paper, *A* and *B*, covered with paraffin (to prevent the paper from being softened by the water). By moving *A* all the way across the tray into the position *C*, all impurities present on the surface of the water are removed. The second strip, *B*, now lies on the perfectly clean surface. A drop of oil, obtained by dissolving a measured quantity of oleic acid in benzene, is allowed to fall on the surface of the water between the two strips. When the benzene has evaporated, a film of oleic acid remains behind. Care is taken to choose a proper amount of oil, so that the latter only partly fills the space between the two strips. The strip *B* is moved in the direction of *A* (Fig. 17*b*) until the oil film just covers the area between the strips (Fig. 17*c*). To distinguish the oil-covered area from the clean water surface, a little talc powder is sprinkled upon it. By blowing gently, at an angle, upon the surface, the talc is made to collect on the oil film so that its surface can be plainly recognized.

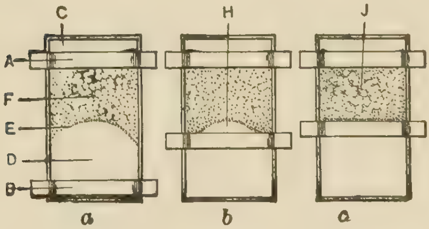

Fig. 17.

Langmuir measured the area covered by the oil. Thus he knew, on the basis of Rayleigh's theory, the area covered by a given number of oleic acid molecules. The number of molecules was found by dividing the weight of acid used (50 mg. in his experiments) by the molecular weight of the acid, and then multiplying the quotient by 61×10^{22}.

What happens in these experiments may be best compared to the situation shown in the sketch, Fig. 18. Let us imagine a number of marbles placed in a large tray (Fig. 18*a*). By pushing the marbles toward each other by means of a movable partition, we bring about the state of affairs indicated in Fig. 18*b*. By moving the partition still farther toward the left, we get the condition shown in Fig. 18*c*. The behavior of the marbles in Fig. 18*b* is similar to the position of the oil film as represented in Fig. 17*c*.

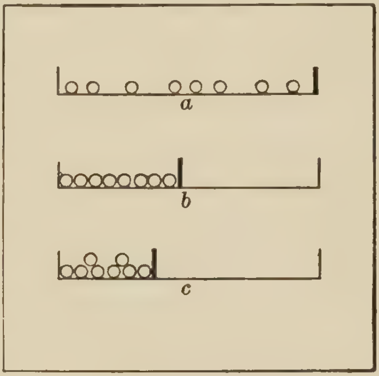

Fig. 18.

By sharply distinguishing between the different conditions shown in Fig. 17, Langmuir was able to perfect the method of Devaux. By means of a special balance, a method was developed which enabled him to measure the force acting on the strip *A* (see Fig. 17) as a function of the area between *A* and *B*, containing the oil film. *B* is kept in its position by weights placed on the pan. The results of these measurements can be represented by curves of the type drawn in Fig. 19.

The forces exerted on *A* (equal to the weight placed on the pan to keep the float *B* in position) are plotted as ordinates, while the corresponding areas are plotted as abscissae. Starting from the right, viz., the region of large areas, we notice that no force is required to keep the float in place. At the point *S* we find that it suddenly becomes necessary to apply a rapidly increasing force (from *S* to *H*) for a slight decrease in area. Beyond the point *H* no further increase in force is necessary to decrease the surface of the oleic acid. From here on, the curve runs practically in a horizontal direction.

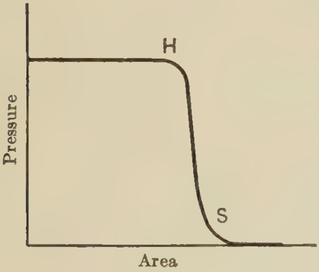

Fig. 19.

It is clear that the first part of the curve, as far as *S*, is comparable with the situation of Fig. 18*a*. At the point *S* the molecules practically touch each other. Between *S* and *H* the monomolecular film undergoes its maximum compression, and further decrease in area causes the appearance of a second layer of molecules, as in the situation sketched in Fig. 18*c*. Numerous determinations by LANGMUIR always gave the same results. More precise measurements by ADAM,[40] who worked with various organic substances under different conditions, in the same type of apparatus as used by LANGMUIR, led to results which were invariably the same. The gradual curvature below *S* may be explained as follows: The fatty-acid molecules on the surface are subjected to a movement of heat; hence, the film which is not yet completely compressed acts as a two-dimensional gas; in other words, the heat motion exerts a pressure in two dimensions. The curved part, therefore, indicates the force which is required to compensate this pressure whenever the area of the film is reduced. It is evident that the curvature below *S* follows an equilateral hyperbola as expressed by BOYLE's law, since the product of the force exerted and the surface is constant.

These measurements again confirm the existence of a monomolecular layer consisting of a known number of molecules. The diameter of a molecule is found by dividing the area by the number of molecules; while the length of a molecule, perpendicular to the oleic acid-water interface, is derived from the quotient of volume and area.

The dimensions of an oleic acid molecule, in the direction parallel to the interface and in the direction perpendicular to it, differ considerably. If the molecules were not oriented, this result would be inexplicable. Furthermore, it would not be clear why oleic acid *spreads* upon a water surface. These experiments and others have shown that only those substances that have an electrically polar group show this phenomenon. A saturated hydrocarbon, for instance, does not expand in the shape of a monomolecular layer but stays on the water as a rather flat drop. It appears, therefore, that the polar group is attracted by the water and that the oleic acid molecules float upon the water with their long dimension vertical.

Some results of LANGMUIR's investigations are given in Table III. It may be seen that he studied acids differing in the length of their chains of carbon atoms. The second column gives the number of carbon atoms in the molecule; the third shows the diameter of the cross section parallel to the interface; while the last column tabulates the calculated length of the molecules, expressed in millimicrons ($1 \mathrm{m}\mu = 10^{-6}$ mm.). In spite of the difference in length, the cross section of all molecules is the same, viz., 0.5 mμ. The length, however, depends on the number of carbon atoms in the chain. These results have been confirmed by the numerous investigations of ADAM.[41]

TABLE III

Acid used	Number of Carbon atoms	Diameter of cross section in mμ	Length in mμ
Palmitic acid.......	C_{16}	0.46	2.4
Stearic acid........	C_{18}	0.47	2.5
Cerotic acid........	C_{26}	0.50	3.1
Myricyl alcohol....	C_{30}	0.52	4.1

Following an entirely different train of thought, W. D. HARKINS [43] arrived at similar conclusions: If a column of water with 1 sq. cm. of cross section (Fig. 20) is pulled in two, there are formed 2 sq. cm. of new surface. Since the surface tension of water is 73 dynes, the work necessary to pull the liquid apart is 2 × 73 ergs. Reunion of the two halves results in the liberation of these 146 ergs; hence the work of *cohesion* (W_c) for water amounts to 73 ergs per square centimeter.

If we divide a column of benzene (with a surface tension of 28 dynes per square centimeter) having the same cross section, into halves, the work of separation is 2 × 28 ergs, and restoration of the original column sets free 56 ergs. Therefore, W_c is here 28 ergs per square centimeter.

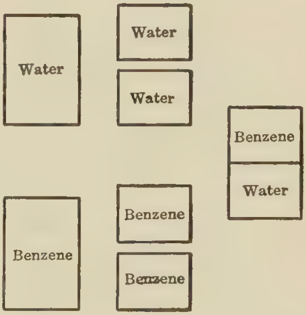

FIG. 20.

If one-half of the benzene layer is placed on top of one-half of the water layer, we obtain a benzene-water interface with an interfacial tension σ_{LL} = 35 dynes per square centimeter. In order to break the new column at the interface, there would be required an amount of work equal to 73 + 28 − 35 = 66 ergs per square centimeter; hence the work of *adhesion* (W_a) for water-benzene equals 66 ergs. The work necessary to separate the two phases is, therefore, considerable; a great amount of potential energy must be overcome to break the contact. The question arises: What is the nature of this potential energy? HARKINS infers that it is the energy required to keep the molecules oriented in a definite position. Polar groups always orient themselves *away from the air toward the water.* Polar groups obviously include, first of all, ionogen groups, such as the carboxyl radical, and also groups containing oxygen, nitrogen, sulphur, or halogens, viz., $-OH$, $=O$, $-NH_2$, $-SH$, etc. These polar groups possess electric stray fields, and the free energy is a minimum when these stray fields occur in a space containing other polar molecules, whereby mutual compensation takes place. It may be stated in this connection that water has a very pronounced polar character.

Data on aliphatic substances in particular give a good foundation for these premises. Let us see, for instance, what the cohesion is for hydrocarbons and their derivatives in which an end carbon atom is substituted. The value of W_c in ergs is as follows:

hydrocarbons: for all around 45
monochlorides: for all around 47
alcohols: for all around 55
monocarbonic acids: for all around 57

With respect to the adhesion of these substances to water, we find that their W_a toward water is:

hydrocarbons: for all around 44
monochlorides: for all around 81
alcohols: for all around 92
monocarbonic acids: for all around 95

These figures give rise to the following considerations:

If a hydrocarbon column is broken into halves, no orientation takes place, for the reason that there are no polar groups present. The result is that W_c is exceedingly low. If, however, there is a polar group present in the molecule, orientation occurs and some energy is required. But at the place of rupture the molecules of the boundary layer orient themselves with their non-polar hydrocarbon chains turned toward the air and the polar ends pointing in the direction of the liquid; hence we separate two non-polar parts, which exert little attraction on each other, and consequently W_c is raised comparatively little (*cf.* Fig. 21 *a* where the small circles represent the polar groups and the narrow bands stand for the hydrocarbon chains).[44]

The separation of hydrocarbons from water takes place likewise without orientation, because there is no directing polar group present in the hydrocarbon; hence W_a for hydrocarbons is approximately equal to W_c. The situation is, however, completely different in the presence of a polar group, as is the case with alcohols, acids, etc. These groups turn toward the water, and a rupture of the interface implies that the attraction of polar groups must be overcome. Inspection of the above figures shows that in those cases W_a is about 70 per cent higher than W_c (*cf.* Fig. 21*b*; the slight solubility of these higher alcohols in water is indicated by the small number of alcohol molecules in the water phase).

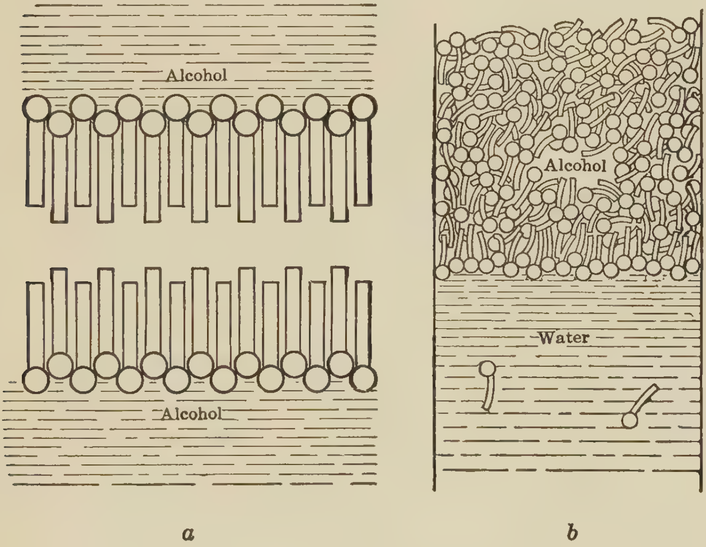

Fig. 21.

The polar character of double bonds is brought out by the fact that W_a is higher for unsaturated hydrocarbons than for the corresponding paraffins ($W_a = 43.8$ for octane and 72.9 for octylene).

The benzene molecule, with its three conjugated double bonds, apparently lies flat on the surface of the water. We can, furthermore, anticipate the results of substitution of polar groups in the benzene nucleus, and the data obtained by HARKINS are in excellent agreement with these expectations. A detailed account, however, falls outside the scope of this book.

From the standpoint of HARKINS' orientation theory, we can readily understand several other facts. A polar group attached to a short hydrocarbon chain (for instance, in methanol, ethanol, acetic acid, etc.) attracts the water so strongly that the hydrocarbon chain is dragged down into the water; hence these compounds are completely miscible with water. If the length of the hydrocarbon chain is considerable, the attraction is insufficient and, as a result, we find that the higher alcohols and fatty acids are partially miscible or practically insoluble in water. Only the polar groups of the molecules in the interface "dissolve" in the water, i.e., are immersed, oriented toward the water.

It also becomes quite clear why W_a is the same for all (higher) alcohols: the interface on the alcohol side always consists of OH groups and, on separating the layers, we do not, so to speak, pull the water away from the different alcohol *molecules* but from a layer of OH radicals, which is the same for all alcohols.

Furthermore, the reason why polar organic compounds accumulate, i.e., are strongly adsorbed, in boundary layers, now becomes apparent. Let us consider, for example, a layer of benzene placed on water. On adding butyric acid to the system, we notice that this substance dissolves to a large extent in the benzene (organic substances generally are quite soluble in organic solvents), but only slightly in water, in spite of the fact that its COOH group is attracted by the water. Consequently, however small the concentration of the acid may be in the benzene layer, the butyric acid molecules move preferably toward the boundary layer where part of the molecule, viz., the carboxyl group, can remain in the water, and the rest, i.e., the hydrocarbon chain, in the organic solvent. The result is, therefore, accumulation of the butyric acid in the interface, in other words, strong adsorption.

The adsorption layer thus becomes a typical transition layer: the two media are separated by an intermediate layer which consists of a hydrocarbon radical on one side and a carboxyl group on the other. As a confirmation of the ancient adage "*similia* *similibus solvuntur"* (like dissolves like), each part of the molecule dissolves in the medium that is like it.

These conclusions will be very helpful in the elucidation of several colloid-chemical phenomena (for instance, those discussed on pp. 106 and 208).

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CHAPTER III

CAPILLARY ELECTRICAL PHENOMENA

12. The Capillary Electrode.—The term capillary electrical phenomena will be used here for those cases in which electromotive forces are influenced by processes that take place in the boundary layer and are related to surface tension and adsorption phenomena. The best-known example in this field is the capillary electrometer, a convenient form of which is shown in Fig. 22. It is based on the following principle:

Two mercury electrodes, *a* and *b*, are connected by means of dilute sulphuric acid. One electrode has a large flat surface, while the other, which touches the sulphuric acid in a capillary tube, has a strongly curved meniscus. When a potential difference is set up between the two electrodes, capillary phenomena must take place at the mercury-sulphuric acid boundary. The interfacial tension, σ, will be lowered by applying electricity to the surface of the electrically uncharged mercury. This is readily understood when we realize that surface tension is the result of mutual attraction of surface elements; addition of an electric charge causes a repulsion of surface elements; hence any electric charge (whether positive or negative) will cause lowering of the surface tension. If, then, by charging the mercury, the surface tension is lowered, the mercury will descend in the capillary. When the movement of the mercury surface is observed through a microscope, the instrument sketched in Fig. 22 serves as a very useful electrometer. For a good understanding of the capillary electrode, we should know that the mercury already has an initial positive charge with respect to the sulphuric acid, as is easily seen from NERNST'S theory of solution pressure. Before the applica-

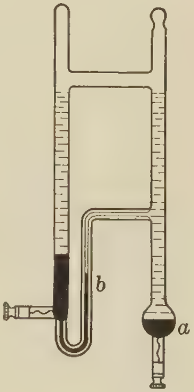

FIG. 22.

tion of an electrical tension the electrode is already charged; hence the addition of a larger positive charge will bring about a *lowering* of the mercury level, while the addition of negative electricity will act in the sense of lowering the electrical tension, and hence the mercury will *ascend*. If the added charge just balances the existing charge the surface tension will be a maximum. Further addition of negative electricity will cause lowering of the meniscus. This is graphically expressed in Fig. 23. It follows that a maximum in the electro-capillary curve is characteristic of the uncharged condition of an electrode, thus permitting the absolute measurement of another.[1] In recent years, FRUMKIN[2] has carried out a number of important investigations dealing with the influence of added substances on the shape of the electro-capillary curve. The changes thus brought about can be ascribed to the orientation of the molecules in the boundary layer in accordance with the theories of LANGMUIR–HARKINS.

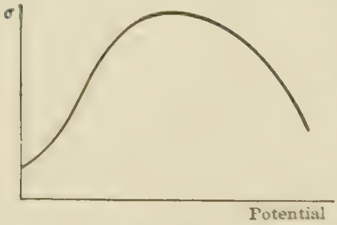

FIG. 23.

13. Capillary Electrical Phenomena.—There are four more phenomena in which electrical potentials occur as a result of peculiar conditions in the boundary layers. These potentials can be increased or decreased, depending on phenomena which are evidently closely connected with those of adsorption and colloid chemistry. The phenomena referred to are as follows: electro-endosmosis; potential of flow (also called streaming potential); cataphoresis; and migration potential (potential of moving particles, or DORN effect).

The remarkable thing about these phenomena is that they occur at boundary faces not involving any metals, and consequently differ considerably from potentials of a galvanic nature.

Electro-endosmosis is the phenomenon that takes place when we dip a porous pot, filled with water, into a large volume of water, and apply a potential difference between the liquids inside and outside the pot. It appears then that a flow of liquid occurs in the direction of the negative electrode (Fig. 24).

Potential of flow or *streaming potential* is the counterpart of electro-endosmosis. If water is forced through the walls of a porous pot, a potential difference is set up between two electrodes placed on either side of the porous wall, as a result of the flow of the water.

Cataphoresis denotes the movement of small particles suspended in a liquid when a potential difference is set up between two electrodes dipping in the liquid.

The phenomenon known as *migration potential* is the converse of cataphoresis. Electrical tensions are set up as a result of the movement of particles through a liquid. Since this motion is difficult to realize, this so-called Dorn effect has been little studied.

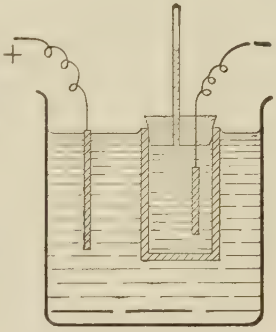

Fig. 24.

A summary of these four phenomena is given in the table below.

TABLE IV

Capillary Electrical Phenomena

Phenomenon	As a result of	Name
Movement of the liquid with respect to the solid wall.	Applied E. M. F.	Electro-endosmosis.
Movement of the wall (of the particle) with respect to the liquid.	Applied E. M. F.	Cataphoresis.
E. M. F. set up.	Flow of a liquid with respect to a wall.	Potential of flow.
E. M. F. set up.	Movement of the wall (of the particle) with respect to the liquid.	Migration potential (Dorn effect).

The last two phenomena are not confined to liquid dispersion media, nor is it necessary that the moving particles be solid. Emulsified drops will likewise behave in this manner. Even when these drops occur in the atmosphere, we may expect these phenomena: By *cascade electricity* we mean, for instance, the

E.M.F. existing between a freely flowing stream of water and the surrounding air.

In the sections that follow, the first three phenomena will be more fully discussed.

14. Electro-endosmosis.—In studying the phenomenon of electro-endosmosis, it is desirable not to operate with a porous pot having a great many capillaries, but to choose a single capillary for performing the experiments. This was done by Elissafoff[3] The method he used is schematically represented in Fig. 25. The movement of the liquid was measured by means of a moving air bubble. To avoid polarization phenomena, the electrodes did not dip into the liquid but were placed in air, close to the ends of the capillary. The large resistance offered by the air necessitated the use of a frictional electrical machine to produce a sufficiently high potential. If we imagine that the process consists in a movement of the liquid with respect to the glass wall of the capillary, as the result of an applied electromotive force, the liquid must have an electric potential with respect to the wall. Evidently, an electric double layer exists at the interface of liquid and wall, as shown in Fig. 26. It is assumed that the negatively charged ions all stick to the wall. Why, in the case of an electrically charged body without pronounced polar character, the wall is always charged negatively with regard to the water, is a question that will be left open for the present. We might imagine that the OH ions of the water are more strongly adsorbed than the H ions, and that consequently a double layer is formed as shown in Fig.

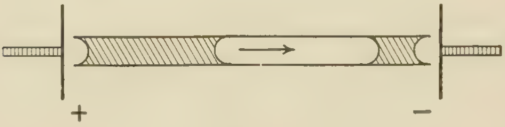

Fig. 25.

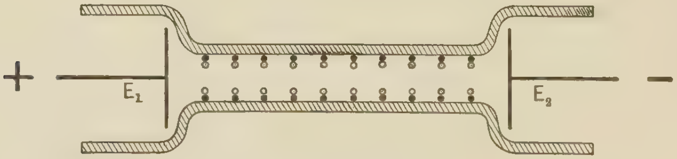

Fig. 26.

26. While this idea will be accepted for the present, the matter will be discussed in more detail on page 102.

If a potential difference is applied to the electrodes, the liquid may be considered as being positively charged and hence as moving in the double layer toward the negative electrode.

It goes without saying that, in case the wall has a strongly polar character, the sign of the preferentially adsorbed ion is determined by this polarity. For instance, if the wall is made of a substance with decidedly basic character, it will be charged positively. PERRIN[4] studied the sign of the electro-endosmotic movement for walls of various materials, for instance, of Al_2O_3, which evidently is charged positively with respect to the liquid, with the result that the latter flows toward the anode. Fig. 27 gives an idea of the conditions that are supposed to exist at a wall of this material. PERRIN found that, besides this oxide, barium carbonate is likewise positively charged, while sulphur, silicates, and glass acquire a negative charge. Comparatively neutral substances, like naphthalene, carborundum, and cotton, also belong to this group.

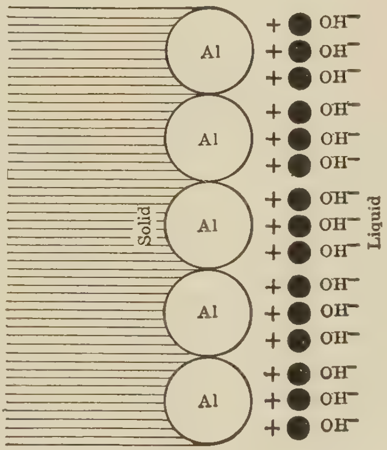

FIG. 27.

In colloid chemistry, we are interested, first of all, in the effect of electrolytes on electric behavior (see p. 9). The investigations of PERRIN, and, more especially, those of ELISSAFOFF brought out the fact that the ion that carries a charge opposite to that of the wall determines the effect of the added electrolyte. The greater the valence of this oppositely charged ion, the stronger its discharging effect on the electric double layer; the valence of the ion of like charge plays a subordinate part.

This rule holds, however, only for simple *inorganic* ions, with the exception of the heavy metals, which behave similarly to organic ions by exerting a much stronger discharging effect; the same is true of the hydrogen ion and the hydroxyl ion. Furthermore, Elissafoff found that the charge of the wall could be easily reduced to practically zero by electrolytes but that a reversal of the charge could seldom be accomplished. In the table below are given some of Elissafoff's results.

TABLE V

Velocity of the Electro-endosmotic Movement

Electrolyte	Concentration in μ-moles per liter *						
	0	5	10	20	50	225	4000
NaCl	50	48	46	44	38	26	5
$\frac{1}{2}K_2SO_4$	50	47	44	41	......	26	8
HNO_3	50	48	......	29	23		
$AgNO_3$	50	40	32	29	27		
Crystal violet	50	......	......	29	4	+	
$BaCl_2$	50	43	......	29			
$\frac{1}{2}Al_2(SO_4)_3$	50	20	5	3	0		
$Th(NO_3)_4$	50	4	+				
NaOH†	50	......	......	99	99		

* 1 μ-mole (micromole) $= 10^{-6}$ mole.

+ Means that the liquid flows towards the + electrode.

† With quartz capillary.

The monovalent ions listed in the table lower the negative charge of the glass wall to practically the same extent, irrespective of the anion with which they are paired. On the other hand, we see that the cation of a heavy metal, like silver, discharges more strongly than sodium. Likewise, the hydrogen ion has a stronger discharging effect than that which would correspond to its valence. The hydroxyl ion, although naturally combined with a cation, occupies an exceptional position regarding capillary electrical processes by imparting a negative charge far exceeding the positive charge imparted by the sodium ion. The hydroxyl ion furthers the process of electro-endosmotic movement quite noticeably. Organic ions appear to have an exceedingly high discharging power.

All these results strongly confirm the impression that we are dealing here with adsorption processes. We saw, for example, on page 35 that all inorganic substances, with the exception of the heavy metals, the H and the OH ion, are slightly adsorbed, while, on the other hand, organic substances, especially polycyclic compounds, are quite strongly adsorbed. The same order evidently comes to light when we study the discharging effect of ions.

Furthermore, it is interesting to note that some of these ions are able to reverse the charge of the double layer; it appears, for instance, that the Th^{++++} ion, in concentrations exceeding 10 μ-moles, turns the negative charge of the capillary into a positive one. The organic ion of crystal violet has the same effect. Hence a strong discharge may lead to a reversal of the initial charge.

Experiments on electro-endosmosis may be readily performed with the capillaries found in a small cylinder of compressed powder, as was done in some early work of Perrin [4] and in a recent interesting investigation by Labes.[5]

15. Flow Potential.—This phenomenon, too, is preferably studied with the aid of a capillary tube instead of a porous pot. When water is forced through the tube an electromotive force is set up between two electrodes placed on either side of this capillary. The investigation is suitably carried out in an apparatus of the type shown in Fig. 28. Comparatively high potentials can be obtained. For instance, when using water prepared for conductivity experiments, we find that this potential amounts to about 25 volts for each atmosphere of pressure exerted on the liquid.

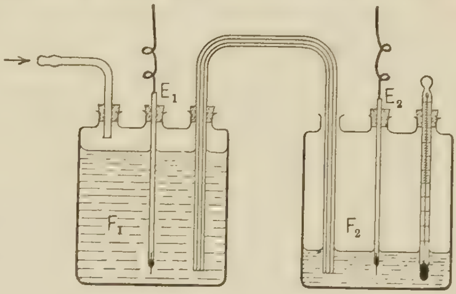

Fig. 28.

Kruyt [6] has made a study of the effect of dissolved electrolytes on these flow potentials. His results are given in Table VI and represented graphically in Fig. 29. The flow potentials are expressed in millivolts per centimeter mercury pressure: E/P. We notice that added electrolytes reduce the flow potential. Since the liquid flows toward the negative electrode, it is positively charged with respect to the wall of the capillary; hence, the cation is the one that has a charge opposite to that of the wall. Here again, the influence of the valence of this ion is quite evident. At the same time, it is seen that the triple charge of the aluminium ion is capable of reversing the charge. Hydrogen ions and organic cations, however, have a much greater effect than corresponds with their valence.

TABLE VI

FLOW POTENTIALS

Electrolyte	Concentration μ-moles per liter	Potential in millivolts / Pressure in cm. mercury
KCl	0	350
	50	102
	100	57
	250	23
	500	13
	1000	4
$BaCl_2$	0	350
	10	139
	25	79
	50	44
	100	25
	200	9
	1000	1
$AlCl_3$	0	350
	0.5	52
	1	+ 42
	2	+122
	3	+129
	4	+100
	10	+ 52
	100	+ 6
	500	+ 1

Compressed powders can also be used in the study of streaming potentials as was shown in an instructive investigation of Briggs on cellulose pulp.[7]

16. Cataphoresis.—Experiments on cataphoresis give results similar to those mentioned in previous sections.

The sign of the charge of a particle moving under the influence of an electric potential is determined by the nature of the material of which the particle consists. If this has a neutral or an acid character, the particle is negatively charged, while metallic oxides and other substances of a more or less basic character are positively charged.

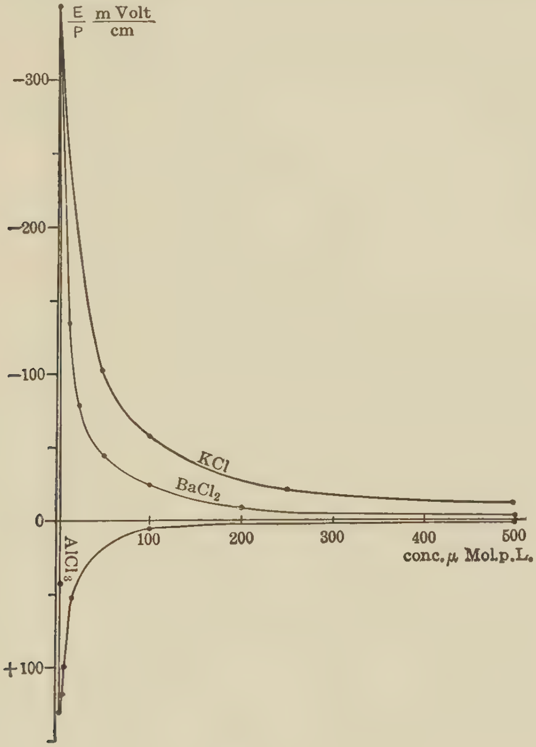

Fig. 29.

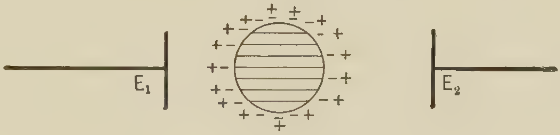

Fig. 30.

Figure 30 represents schematically a particle with its electric double layer, in agreement with the data of the previous sections.

The influence of added electrolytes on particles of an oil emulsion was studied extensively by Ellis [8] and by Powis.[9] Their results are completely in line with the discussion on the preceding pages, and here again the effect of various ions can be related to the manner in which these substances are adsorbed.

The measurement of cataphoretic velocity can be carried out in two ways, which are based on different principles.[10] Whenever it is possible to see a distinct boundary between the colloidal solution and the contact layer of the pure dispersion medium, the migration of the interface under the influence of an electric potential can be measured. This method, therefore, depends on observation of the movement of the particles as a whole. Fig. 31 shows the apparatus used for this purpose, as constructed by Burton.[11] The two electrodes are placed in the pure solvent, which occupies the space above the colloidal solution. The filling takes place through a connecting funnel. Various investigators have modified this apparatus more or less. Measurements by means of this method are subject to several difficulties, and its applicability is limited to sols that are sufficiently colored to enable one to discern the boundary layer. The latter often changes its appearance during the experiment and thus prevents accurate measurements. In some cases it is possible to make the boundary between a colorless sol and the supernatant water layer visible by illuminating the tube with ultraviolet light which causes, for instance, protein sols to fluoresce.[12] Another method is to send a beam of light from above through the tube, thus producing a Tyndall effect in the colloidal solution [10, 13] (see Section 65). The boundary is nearly always disturbed by the products of polarization formed at the electrodes. This makes it advisable to place the electrodes in side tubes fused to the limbs of the apparatus.[14]

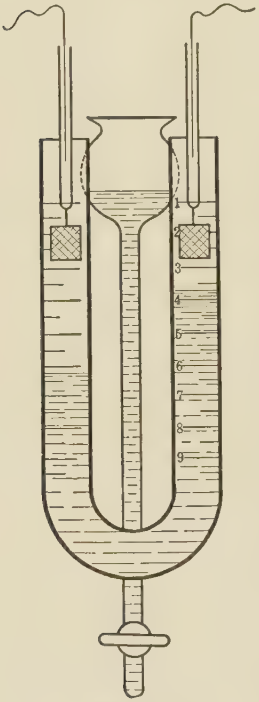

Fig. 31.

The second method consists in the observation of a single particle. The sample is watched under the microscope [15] or else under the ultramicroscope [16] (depending on the size of the particles) and arrangements are made to follow the cataphoretic movement microscopically. The object under observation must be placed between two electrodes. This method has likewise been applied in various forms. The principle is shown in Fig. 32.

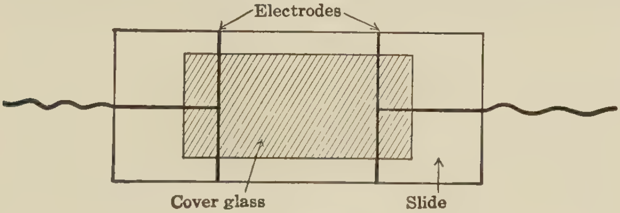

Fig. 32.

Since the particles are in Brownian movement, it is always necessary to take the average of a large number of observations. In this method in particular, and to some extent in the one previously described, a serious complication comes to the fore, viz., the electro-endosmotic flow of the liquid along the walls of the container in which the cataphoretic movement of the particles is observed. For instance, if negatively charged particles fill the space between the glass walls, the particles move toward the anode, while the liquid flows along the walls toward the cathode, as stated in Sec. 14. This flowing liquid carries particles along; as a result, we get, starting from the wall, first particles moving in one direction, then stationary particles, and in the center particles flowing in the opposite direction (Fig. 33). Observations taken at various distances from the wall enable us, however, to calculate the true cataphoretic velocity.[17]

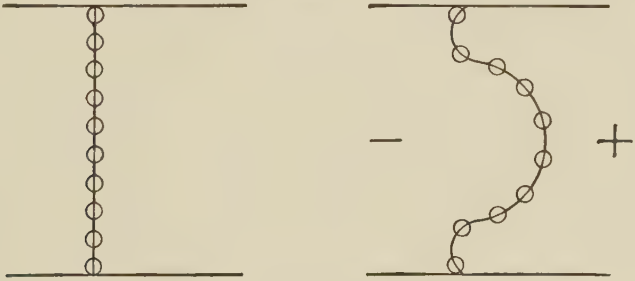

Fig. 33.

17. Migration Potential (Dorn effect).—The movement of particles may be brought about by the force of gravity. We then measure the potential difference between an electrode placed at the top and another one placed at the bottom of the column of liquid through which the falling particles are moving. This method is difficult to carry out and has as yet given purely qualitative results. One of the most recent investigations is that of Burton and Currie.[18]

18. Charge and Potential.—On page 54 we assumed the existence of an electric double layer—a concept introduced by Helmholtz—in order to explain capillary electrical phenomena. Later (on p. 97) we shall see to what extent this explanation holds.

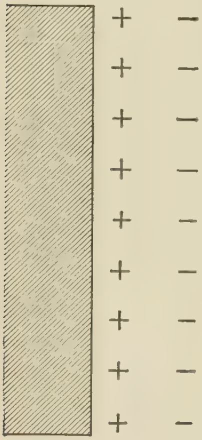

Fig. 34.

If a wall (as represented in Fig. 34) carries an electric double layer, it may be said that the positive charge e of the wall is due to the positive ions of the inner coating (starting from the wall) while the outer coating carries an equal charge of opposite sign. Both layers taken together form, in reality, a condenser. Between the plates of this condenser there exists a potential difference E for which the following relation holds:

$$E = \frac{4\pi\delta}{D}e$$

Here δ and D refer respectively to the distance between the plates and the dielectric constant of the medium. Since E and e are proportional quantities in case δ and D are constant (as is frequently assumed), it seems permissible to use the expressions "charge of the wall" and "potential of the double layer" (viz., potential difference between the coatings of the double layer) interchangeably. For the present, we shall apply these customary simplifications with a clear understanding of the arbitrariness of certain assumptions (for which see Sec. 32).

In Chapter VI it will be shown that in colloid chemistry the potential of the double layer is a more fundamental quantity than the charge of the wall. For didactic reasons, however, we shall continue to employ the term "charge" and indicate later what reservations must be made to justify the use of this term.

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PART II

Suspensoids

CHAPTER IV

STABILITY OF SUSPENSOIDS

19. Charge and Stability.—The fact that colloidal systems placed between two electrodes show the phenomenon of cataphoresis was first firmly established in 1892 by Linder and Picton.[1]

Burton,[2] while investigating this phenomenon in 1906, studied the influence of an added aluminium salt on the cataphoretic velocity of the particles of a gold sol, and showed how, at the same time, the stability of the sol changes. In the table below, these results are reproduced.

TABLE VII

Milligrams Al per liter	Cataphoretic velocity in μ per volt per cm. per sec.	Property of the sol
0	3.30 (towards anode).	Indefinitely stable.
0.19	1.71 (towards anode).	Flocculated after 4 hours.
....	0	Flocculated immediately.
0.38	0.17 (towards cathode).	Flocculated after 4 hours.
0.63	1.35 (towards cathode).	Not yet completely flocculated after 4 days.

It is seen that the cataphoretic velocity at first decreases when aluminium chloride is added, is then reduced to zero, and on further addition increases, obviously because of a reversal in the charge of the particles. The last column of the table shows that the stability of the sol decreases as the cataphoretic velocity diminishes, while the uncharged particle is apparently completely robbed of its stability.

These experiments of Burton confirm the results obtained by Hardy [3] in 1900, which had been vigorously opposed in the intermediate years.[4] Hardy found that the sol of denatured egg albumin, i.e., the sol of well-dialyzed egg albumin which has been transformed by heating into denatured albumin, undergoes different changes, depending on whether acid or alkali is added to the sol. With acid the sol is positively charged and stable; with alkali it is negative but likewise stable. In the absence of either, *the sol flocculates.*

On the basis of these experiments, Hardy had already expressed the opinion that a colloidal solution can only be stable when the particles possess an electric charge. Deprived of their charge, the particles unite to form flakes which separate from the sol. The flocculation, according to Hardy, takes place at the *isoelectric point.*

Later investigations of Powis [5] have indicated, however, that it is not necessary to deprive the particles *completely* of their charge in order to bring about flocculation. A *lowering* of the potential of the interface to a certain characteristic value, which Powis calls the *critical potential,* is sufficient to produce flocculation. A certain oil emulsion showed a potential difference in the electric double layer amounting to 46 millivolts. Lowering of this potential to 30 millivolts caused the oil drops to unite in such a way that separation from the water resulted. Corresponding results have been obtained for various other sols.[6]

The data obtained by Hardy, Burton, Powis, and others have an important bearing on colloid chemistry, and particularly on suspensoids. For this group of colloids, it has been clearly demonstrated that the stability of the sol is governed by the electric charge of the particles. The condition of such a sol, and the manner in which its stability is destroyed, may be represented as follows:

We are dealing with colloid particles which are protected, by the electric charge of the double layer, against actual collisions. The particles are in a state of vigorous motion and approach one another repeatedly, but the spheres of their electric potential do not penetrate one another on account of their equal signs. These prevent the action of the superficial forces at the boundary of the particles and hence the particles cannot unite. The more the electric charge of the particles is decreased, the smaller the interference. If no charge were present, each collision would result in a union. Under those circumstances the "*probability of adhesion*" of the particles, i.e., the ratio of the number of adhesions to the total number of collisions, would be one. In case the potential of the boundary layer possesses a certain value, the collisions will, as a rule, be without results. Only particles that happen to have a high speed will be able to penetrate the repelling sphere and cause adhesion.* In that case the probability of adhesion will have a value between 0 and 1.

The mechanism of flocculation is, therefore, determined by the *probability of collision* and the *probability of adhesion.* The former depends mainly on temperature and concentration; the latter, in the case of suspensoids, obviously on the electric charge.

The principle of HARDY and POWIS, consequently, applies only to those colloids for which the probability of adhesion is exclusively a function of the electric charge.

Elsewhere in this book we shall see that the probability of adhesion in the case of emulsoids depends on one more factor. The opposition which HARDY encountered had its origin in the study of colloidal systems in which the probability of adhesion did not depend *solely* on the electric charge.

Most investigations dealing with the influence of electrolytes on the stability of a sol consisted in the determination of the so-called limiting values (also known as flocculation or precipitation values). By limiting value is usually meant the number of millimoles of electrolyte per liter necessary to precipitate the sol completely in a stated time. It is customary to compute the concentration for the total volume of sol plus added electrolyte.

To determine the flocculation value, one may place 10 cc. of sol in each of a number of small beakers, and then add to each 10 cc. of electrolyte solution. These electrolyte solutions are made up beforehand in different concentrations. At the end of a definite time one ascertains in which cases complete precipitation has occurred. A second series is then started, with concentrations ranging from that of the last beaker showing incomplete flocculation to that of the first in which complete precipitation occurred.

The most suitable time for ascertaining the flocculation depends on the nature of the sol. In general, the conditions are chosen in such a way that the results are easily reproduced. To this end it is not sufficient merely to make observations after a fixed period, say, one or two hours, but the same method of adding and shaking should be followed each time.

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* The average velocity depends, of course, on the temperature, but the numerical value of the velocity of a given particle is accidental, in accordance with MAXWELL's distribution law as will be further discussed in Sec. 43.

It is not certain that this method of determining the precipitation value will exactly realize the condition of the critical potential. However, experiments dealing with the speed of flocculation (to be discussed on p. 121) have shown that the potential of the particles in a beaker that shows complete flocculation agrees fairly closely with the critical potential, and if it varies at all it differs only by a small constant amount.

Table VIII gives the flocculation values for the As_2S_3 sol [7] and for the gold sol.[8]

TABLE VIII

FLOCCULATION VALUES

Electrolyte	Flocculation value in millimoles per liter		Electrolyte	Flocculation value in millimoles per liter	
Monovalent cations	As_2S_3	Au	Divalent cations	As_2S_3	Au
LiCl	58	......	$MgSO_4$	0.81	
NaCl	51	24	$MgCl_2$	0.72	
KCl	50	......	$CaCl_2$	0.65	0.41
KNO_3	50	25	$SrCl_2$	0.63	
$\frac{1}{2}K_2SO_4$	63	23	$BaCl_2$	0.69	0.35
			$ZnCl_2$	0.68	
			$(UO_2)(NO_3)_2$	0.64	2.8
HCl	31	5.5	Quinine sulphate	0.24	
$\frac{1}{2}H_2SO_4$	30		Benzidine nitrate	0.09	
Aniline chloride	2.5		$CuSO_4$	......	0.015
Strychnine chloride	0.5		$PdCl_2$	......	0.007
Morphine chloride	0.4	0.54	$Pb(NO_3)_2$	......	0.002
Crystal violet	0.16				
New fuchsin	0.11	0.002			
Trivalent cations			Tetravalent cation		
$AlCl_3$	0.093	......	$Th(NO_3)_4$	0.090	
$Al(NO_3)_3$	0.095				
$\frac{1}{2}Al_2(SO_4)_3$	0.096	0.009			
$Ce(NO_3)_3$	0.080	0.003			

Looking over the figures in large type, we find the following facts. Both sols are negatively charged; the added anion, which also has a negative charge, apparently plays a subordinate rôle in the flocculation process. On the other hand, the valence of the cation governs, to a large extent, the flocculating power of the added electrolyte. In the case of the As_2S_3 sol, we notice that all three alkali metals give a flocculation value around 50 millimoles, and the alkaline earths a value approximating 0.68 millimole, while aluminium and cerium give values in the neighborhood of 0.1 millimole. A similar order comes to light in the case of the gold sol. This pronounced dependence of flocculation on valence is often called the SCHULZE–HARDY rule (*cf.* p. 170).

The electrolytes printed in small type do not fit into this simple scheme. The hydrogen ion, organic ions, and those of the heavy metals have a greater flocculating power than that which would correspond to their valence.

About twenty years ago FREUNDLICH[9] developed his classical theory which meant to show not only why the flocculating power increases with the valence of the oppositely charged ion, but also why it increases so disproportionately. Assuming the flocculation value, in the case of As_2S_3, for aluminum, to be 1, we find that the value for barium is about 7, and that for potassium over 500. Although, generally speaking, this theory is not correct, it often approaches reality closely and for that reason we still place it in the foreground of our discussions.

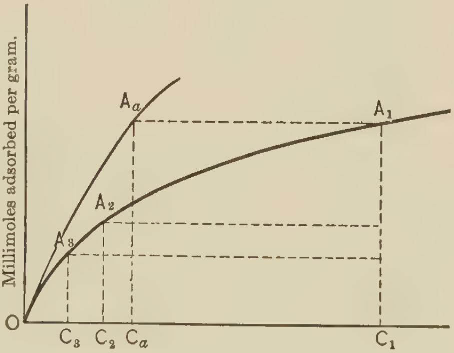

FIG. 35.

FREUNDLICH's line of thought was based on the idea that all inorganic ions of light metals, and likewise the inorganic anions, are adsorbed to the same extent. The heavy adsorption isotherm in Fig. 35 represents, therefore, the common isotherm for all inorganic ions (with the exception of those of the heavy metals). In the graph, the concentrations are plotted in moles per liter as abscissae, while the ordinates express the number of millimoles adsorbed per gram of adsorbent.

On page 59 we saw that a particle showing cataphoresis owes its charge to an electric double layer. When an added electrolyte removes this charge depending on the valence of the oppositely charged ion, it is reasonable to assume that the latter attacks the charge of the double layer, resulting in an interchange of ions (as discussed on p. 40) and a disturbance of the double layer.

If we assume that an amount A_1c_1 (Fig. 35) of a monovalent cation is required to lower the charge * to the critical potential, it is obvious that half that number of moles of a divalent ion (A_2c_2) and one-third that amount ($A_3c_3 = \frac{1}{3}A_1c_1$) of a trivalent ion will be necessary.

The equilibrium concentrations corresponding to these adsorbed quantities, c_1, c_2, and c_3, do not merely decrease with increasing valence, but the peculiar shape of the adsorption isotherm brings about strongly disproportionate concentrations in the liquid when the amounts adsorbed are in simple ratios.

When we are dealing with strongly adsorbed ions, another adsorption isotherm, as drawn on the left in Fig. 35, represents the actual conditions. An amount A_ac_a is now adsorbed at a much smaller concentration, c_a, and the same discharging effect therefore takes place at considerably lower concentration. This explains why the electrolytes printed in small type in Table VIII have much lower floccuation values than other ions of corresponding valence. As we saw previously, the hydrogen ion, organic ions, and those of heavy metals are precisely the ones that are more strongly adsorbed than other ions (see p. 57) and hence must follow an adsorption isotherm with steeper slope. As a matter of fact, it was found by experiment that these ions are adsorbed by As_2S_3 powder in the same order as that in which they are listed with regard to their flocculation values. Table VIII gives the flocculation values for various organic ions; and, as FREUNDLICH was able to show, of these ions, that of aniline chloride is least adsorbed while new fuchsin is adsorbed best of all.

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* The attention of the reader is called to the introduction of an incorrect element in the discussion. On page 62 it was already pointed out that it is not, a priori, certain that in all cases one and the same *charge* has to be removed in order to produce a definite lowering of the *potential* in the double layer. This point will be taken up on page 97.

The last-named ion, viz., new fuchsin, is well adapted for demonstrating that flocculation really takes place by adsorbing the ion of opposite charge. On adding to an As_2S_3 sol, placed in a series of beakers, increasing amounts of a solution of new fuchsin, we observe that the liquid in which complete flocculation occurs becomes colorless and, furthermore, we notice that the precipitated flakes do not show the color of the arsenic trisulphide but are distinctly purple. Flocculation is thus accompanied by precipitation of the colored ion. The chlorine appears to be left in the supernatant clear liquid (see p. 40).

What was said about the stronger adsorbability of organic ions evidently applies also to heavy metals. This was already brought out in Table VIII in the effect of Cu, Pd, and Pb ions on the gold sol. In the case of the sol of arsenic trisulphide, it is difficult to show this phenomenon on account of the hydrogen sulphide present in the dispersion medium, which reacts with the salts of heavy metals. Table IX presents some data for the sol of HgS,[10] which on hydrolysis produces much less hydrogen sulphide. Here again, we notice the powerful flocculating action of the ions of the heavy metals. Morawitz [11] and also Freundlich and Schucht [10] showed that heavy metals are, in fact, more strongly adsorbed than light ones.

TABLE IX

Flocculation Values for the HgS Sol

Electrolyte	Flocculation value	Electrolyte	Flocculation value
Monovalent cations		Divalent cations	
NaCl	13	$SrCl_2$	0.88
KCl	10	$BaBr_2$	0.68
NH_4C_4	10	$UO_2(NO_3)_2$	0.79
$AgNO_3$	0.44	$HgCl_2$	0.11
$TlNO_3$	0.14	$Pb(NO_3)_2$	0.050
$HgNO_3$	0.07	$CuSO_4$	0.047

Our knowledge of capillary electrical phenomena (see Chapter III) leads us to believe that the ion of like charge is not entirely without influence on them, particularly when anion and cation show a striking contrast in adsorbability, or when they differ in

TABLE X

Electrolyte	Flocculation value As_2S_3	Nature of anion
Potassium citrate^{---}	> 240	Organic, strongly adsorbable, polyvalent
acetate^{-}	110	Organic, strongly adsorbable
formiate^{-}	86	Organic, strongly adsorbable
sulphate^{--}	66	Inorganic, divalent
chloride^{-}	50	Normal
nitrate^{-}	50	Normal

valence. In determining flocculation values, we find, for instance, that anions having a strongly negative character raise the flocculation value of a negatively charged sol to a certain extent. In Table X, flocculation values are given for a number of salts the anions of which differ greatly in character. The connection is clear without further comment.

Discharge and flocculation are, in a way, not brought about by the oppositely charged ion alone but by a difference in effect of the two ions[12] whereby, generally speaking, the influence of the ion of opposite charge predominates.

TABLE XI

Flocculation Values for the Fe_2O_3 Sol

	Electrolytes	Flocculation values
Monovalent anions	KI	16
	KNO_3	12
	KBr	12
	KCl	9
	NaCl	9.2
	$\frac{1}{2}BaCl_2$	9.6
	$\frac{1}{2}Ba(OH)_2$	0.4
Divalent anions	K_2SO_4	0.20
	Tl_2SO_4	0.22
	$MgSO_4$	0.22
	$K_2Cr_2O_7$	0.19

Concerning positively charged sols, very similar statements can be made. In Table XI are listed the flocculation values obtained with various salts, for the sol of Fe_2O_3.[13] The monovalent anions form one group, while the divalent belong to another group. The influence of the cation is subordinate in this case. It is immaterial, for instance, whether the chloride is present as sodium chloride or as barium chloride. The differences in flocculation value for these two salts are not in excess of those met in Tables VIII and IX. The OH ion occupies an exceptional position, corresponding to the abnormality presented by the H ion in Table VIII.

The close connection that exists between valence and flocculation value is well illustrated by an investigation of KITCHIMATSU MATSUNO.[14] Precipitating the As_2S_3 sol by complex cobalt salts having cations with different valences, he found that the following concentrations were required:

monovalent complex salt	5000 μ-moles per liter
divalent complex salt	160 μ-moles per liter
trivalent complex salt	22 μ-moles per liter
tetravalent complex salt	5 μ-moles per liter
pentavalent complex salt	(missing)
hexavalent complex salt	0.7 μ-mole per liter

The fact that a value of 5 millimoles is found, instead of 50 (*cf.* Table VIII) for a monovalent salt is due to the different technique followed by MATSUNO. Instead of determining the concentration necessary for complete flocculation, he measured the so-called threshold value, viz., the amount required for *initial* flocculation. This value plays the same part as the ordinary limiting value; but it corresponds to another (lower) equivalent adsorption and another (higher) critical potential, called *first* critical potential, as distinguished from the *second* which we have heretofore called *the* critical potential and which will be so designated throughout the text.

20. Electrolytes Carried Down by the Flocculating Sol.—It was mentioned in Sec. 19 that we could render visible the " carrying down " of the ion of opposite charge for new fuchsin. It is, however, also feasible to follow this ionic precipitation quantitatively.

As early as 1901, Whitney and Ober[15] observed that when an As_2S_3 sol is precipitated with $BaCl_2$ the precipitate contains barium but no chlorine. Before flocculation, the solution contained 0.1675 g. of barium, and afterward 0.1523 g. For the chlorine, the amounts were 0.0865 g. and 0.0863 g., respectively, i.e., practically the same.

This transport of electrolytes enables us to check the theory of Freundlich accurately. Let us first form a mental picture of the mechanism of the flocculation process.

The colloidal particle carries its electric charge in the form of an electric double layer. In Fig. 36 is schematically reproduced the condition of an As_2S_3 particle as it occurs in the sol. We assume that the charge is primarily due to the hydrogen sulphide which has been (either completely or in part) adsorbed in the preparation of the sol. As a result the hydrogen and the sulphur ions are oriented in an electric double layer. The sulphur ions are found on the inside, next to the particle, while the hydrogen ions are located in the outer shell. On the addition of barium chloride the particle preferably adsorbs the barium ions. Consequently, the orientation of the boundary ions is disturbed and the charge disappears. At the same time, the hydrogen ions, no longer attached electrically to the sulphur ions, replace the barium ions in the dispersion medium so that the latter, after the flocculation, has an acid reaction. (*Cf.* p. 108.)

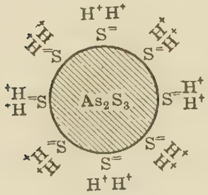

Fig. 36.

Assuming the validity of Freundlich's theory of flocculation (Sec. 19), one might expect that the amounts of cation carried down at the concentration of the limiting value are equivalent for all electrolytes. A lowering of the original charge to the critical value would require a certain amount of electricity of opposite sign, viz., a definite number of gram equivalents of cation. This expectation was, indeed, fulfilled in some cases as can be seen in Table XII.

The last column records the quantities of ion (expressed in milli-equivalents) adsorbed by the precipitates formed when concentrations equal to the flocculation values are added to the sol.

From these data it is seen that, in spite of their widely varying flocculation values, practically electro-equivalent amounts of dif-

TABLE XII

Amount of Cation Adsorbed by the As_2S_3 Sol at the Flocculation Value

Ion	Flocculation value in millimoles per liter	Adsorbed milli-equivalents of cation per 25 g. of As_2S_3
K^+	50	2.05
Aniline$^+$	2.5	1.85
New fuchsin$^+$	0.1	1.90
Ca^{++}	0.6	2.50
Sr^{++}	0.6	2.05
Ba^{++}	0.6	2.15
UO_2^{++}	0.6	2.20
Ce^{+++}	0.09	1.72

ferent cations are adsorbed. Thus, while the flocculation values of potassium and new fuchsin are in the ratio of 500 : 1, the adsorbed amounts differ only by a few per cent.

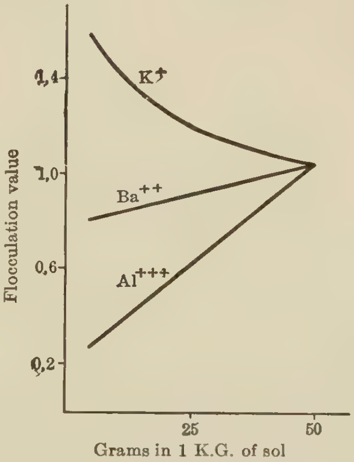

Fig. 37.

An analogous investigation for the HgS sol did not furnish such good results as those presented in Table XII.

On the other hand, experiments carried out on the positively charged Al_2O_3 sol led again to satisfactory results as regards the equivalence of the anions adsorbed at the flocculation values.[17]

This equivalence is, nevertheless, not at all a general phenomenon. In a recent paper by Freundlich, Joachimsohn and Ettisch [18] it was shown to be absent both for the As_2S_3 sol and for the gold sol. The discrepancy between these earlier and the later data will be explained on pp. 101 and 102.

21. Flocculation Value and Concentration of Sol. — The mechanism of the flocculation process becomes more apparent when we examine the manner in which the flocculation value depends on the amount of colloid material present in the sol.[19]

When we prepare As_2S_3 sols by diluting a given sol with water, and then investigate the flocculation values for these sols of different concentrations, we obtain the following results (Fig. 37). The common point indicates the flocculation value for K, Ba, and Al, each time taken as unity. The figure shows that dilution of the sol raises the flocculation value for K, and lowers it for Al, while Ba occupies an intermediate position.

One might be inclined to reason *a priori* as follows:

Let Fig. 38*a* represent schematically a sol of a given concentration.

In Fig. 38*b* the same sol is sketched, having twice that concentration. Flocculation occurs when each particle has adsorbed a certain quantity. This quantity (a) is adsorbed at a concentration χ. Representing the flocculation value in the first case by γ_1 and the number of particles by n, we have:

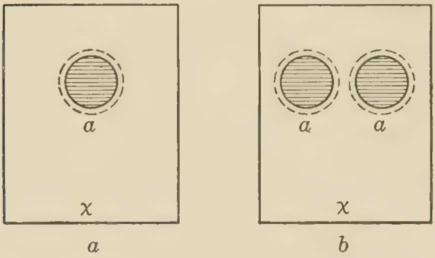

Fig. 38.

$$\gamma_1 = \chi + na;$$

and in the case of Fig. 38, *b*:

$$\gamma_2 = \chi + 2na.$$

Hence, one might expect that, in general, a sol of higher concentration would correspond to a higher flocculation value; or, inversely, that γ would decrease on dilution.

This dependence, however, will be the more strongly felt, the lower the flocculation value. We know that at the flocculation value of a monovalent ion only a small part is adsorbed; hence, na or $2na$ is exceedingly small by comparison with γ. For a trivalent ion, on the other hand, where the flocculation value is quite small, nearly all is adsorbed at that minute value. In that case γ_1 is about equal to na, and a pronounced inter-dependence must exist between flocculation value and concentration.

In Fig. 37 we notice that for Ba and Al the results are in accordance with this line of reasoning. For the monovalent K ion, however, the relationship is just the opposite of what might be expected on the basis of the previous discussion: the dilute sol has a *greater* flocculation value. Another factor has been left out, viz., the fact that dilution of the sol draws the particles farther apart and hence decreases the probability of collision (*cf.* p. 69). If we want to produce flocculation in the same time, we must increase the probability of cohesion in order to compensate for the decreased probability of collision.

The first part of our discussion, in fact, any general consideration of the relation between electric charge and flocculation, must deal with the probability of adhesion while the probability of collision is assumed to be constant.

For monovalent ions, the first-mentioned effect is small, hence the second effect predominates; for the Al ion, the first effect is very pronounced and consequently predominates. The Ba ion takes an intermediate position in which flocculation value and concentration of the sol are just about independent of each other, or rather, γ decreases slightly on dilution.

The relations are, however, not the same for all sols. Sometimes the tendency to raise the flocculation value on dilution of the sol is not confined to monovalent ions but also occurs for polyvalent ions (for instance, in the case of the gold sol).[20] With other sols, e.g., the Fe_2O_3 sol, the tendency to decrease prevails even when monovalent ions are present.[19]

22. Heat Effect and Volume Change on Flocculation.—It is worthy of note that the flocculation of suspensoids takes place with hardly any perceptible heat effect and with little or no volume change. This was already noticed by Linder and Picton [21] (see also p. 169). Kruyt and van der Spek [22] by means of a refined apparatus determined the heat of flocculation of an As_2S_3 sol and found it to be practically nil. Hence the surface energy liberated is so small that it does not give rise to a heat effect. This is due to one of two reasons: either the boundary tension solid-liquid is too small or else (and this is more likely) the disappearing surface is too small in area. There is, indeed, reason to suspect that the agglomeration of the particles occurs only in a few places (*cf.* p. 124). In some cases, noticeable heat effects have been found [23] but Mathews and Browne demonstrated that these resulted mainly from reactions in true solution running parallel with the process of flocculation. Only a small fraction can perhaps be accounted for as a heat of adsorption due to the change of the substances adsorbed during flocculation.

23. Summary.—In the preceding pages it has been stated that the stability of suspensoids depends on their electric charge and that the action of electrolytes is based on a process of adsorption; hence, it is obvious that no stoichiometric relation exists between the weight of precipitated colloid and the amount of electrolyte which causes precipitation. We now clearly understand that the absence of stoichiometric relations, already discussed on page 5, is characteristic of colloidal systems. VAN BEMMELEN, who carried out colloid-chemical investigations between 1870 and 1910, was one of the first to emphasize persistently the absence of stoichiometric relations.

In the foregoing sections, the electric charge of colloids, the definite magnitude of that charge, and the part of the latter which must be removed have been discussed repeatedly. It now becomes necessary to form a quantitative idea about the electric charges of the particles. Although we are familiar with phenomena which are related to these interfacial charges (see Chapter III), our next problem is to find out how, for instance, the cataphoretic velocity depends *quantitatively* on the charge of the particle, what the connection is between the charge of the glass wall and the flow potential, etc. In Chapter V these questions will be further discussed.

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CHAPTER V

CHARGE AND STABILITY

24. Electro-endosmosis and Charge.—Figure 39 represents schematically the movement of a liquid in a tube under the influence of the potential difference between the electrodes. Let us assume that the wall is negatively charged and that, consequently, the positive part of the double layer lies on the side of the liquid. Let E be the potential difference between the electrodes, l the distance between them, ϕ the cross section of the tube, δ the thickness of the boundary layer, and u the electro-endosmotic velocity of a particle of liquid. For the volume v, transported per second, we have:

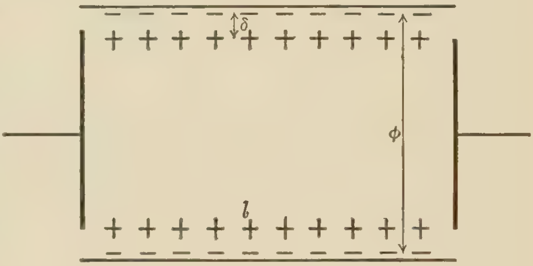

Fig. 39.

$$v = \phi u. \qquad (1)$$

The electric force overcomes the friction and thus originates the velocity u. The force of friction is proportional to the viscosity η and to the drop in velocity $\frac{du}{dx}$, dx denoting the distance of a particle from the wall. Since the velocity of the liquid elements of the liquid is u, and since the negative side of the double layer is supposed to be at rest, there exists in the boundary layer a velocity gradient from u to zero over a distance δ. We may therefore assume that:

$$\frac{du}{dx} = \frac{u}{\delta}.$$

The force of friction then becomes equal to $\eta \frac{u}{\delta}$, or, according to equation (1) $\eta \frac{v}{\phi \delta}$. For a potential difference E and a distance l between electrodes, the potential gradient $H = \frac{E}{l}$. If we call the quantity of electricity per square centimeter of wall e, the electric force operating per unit area is He. When frictional force and electric force are equal we can write:

$$He = \frac{\eta v}{\phi \delta};$$

or,

$$e = \frac{\eta v}{H \phi \delta}. \quad \ldots \ldots \ldots \quad (2)$$

The electric double layer may be likened to a condenser since in this case we have a negatively charged layer and a positively charged layer at a distance δ from each other. For such a condenser the following relation holds:

$$\zeta = \frac{4\pi \delta e}{D}, \quad \ldots \ldots \ldots \quad (3)$$

where ζ designates the potential in the double layer and D the dielectric constant of the medium separating the layers. If i denotes the strength of the current, κ the specific conductance of the liquid, and W the total resistance between the electrodes, we have, according to Ohm's law:

$$H = \frac{E}{l} = \frac{iW}{l} = \frac{i \frac{l}{\kappa \phi}}{l} = \frac{i}{\kappa \phi}. \quad \ldots \ldots \quad (4)$$

Substituting the values for H (equation 4) and e (equation 2) in equation (3), we get:

$$\zeta = \frac{4\pi}{iD} \cdot \eta \cdot \kappa \cdot v.$$

The foregoing derivation thus furnishes a connection between the potential of the double layer, ζ, and the volume transported per second, v, the remaining terms of the equation being accessible to direct measurement.

25. Cataphoresis and Charge.—If u denotes the cataphoretic velocity, there must be, as in the preceding section, equilibrium between frictional and electrical force; hence:

$$\eta\frac{u}{\delta} = He \quad \text{or} \quad \eta\frac{u}{\delta} = \frac{E}{l}e,$$

where the letters have the same meanings as in Sec. 24, except that u stands for the velocity of the particle.

Replacing e on the right-hand side of the equation by the value derived from the formula for electric condensers, we obtain:

$$u = \frac{\zeta ED}{4\pi\eta l} \quad \text{or} \quad \zeta = \frac{4\pi l}{ED}\eta u = \frac{4\pi\eta}{HD}.u. \quad . \quad . \quad . \quad (5)$$

It was recently brought out by Debye and Hückel[1] that for a *spherical* particle the factor 4 in these equations should be 6.

This formula indicates that for a given potential difference, E, there is a direct proportion between the potential of the double layer and the cataphoretic velocity, u. The values substituted for η and D in the proportionality constant are commonly those determined for pure water. In studying the cataphoretic velocity of sols at different concentrations of electrolyte, we are not justified to do so unless η and D remain the same when the concentration is varied. The electrolyte concentrations that play a part in colloid chemistry are so small that their effect on η can no doubt be neglected. For D, this is not always the case as will be seen further on (see p. 88).

26. Flow Potential and Charge.—As detailed derivations were given in the two preceding sections we can dispense with the derivation here and merely mention the final result:

$$\zeta = \frac{4\pi}{D}\eta.\kappa\frac{E}{P}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where κ is the specific conductance, E the flow potential, and P the pressure under which the liquid is forced from one side of the capillary to the other. In deriving this formula we assume that the law of Poiseuille is applicable to the flowing liquid.

27. Measurements of Boundary Potentials.—Measurements by the author[2] have shown that the flow potential of pure water is lowered by the addition of electrolytes (see p. 58). However, if one calculates, by means of equation (6), the potential in the boundary layer at the glass wall, it will be found, contrary to expectation, that the charge does not decrease with the concentration. This can be accounted for by the fact that, in the formula, E decreases, while κ increases, with the concentration.

Figure 40 illustrates the change of the boundary potential with the concentration for various ions. Small quantities of an electrolyte having a monovalent or divalent cation raise the boundary charge. Since this increase is due to the negative ion, the influence of the latter in minute concentrations seems to exceed the discharging effect of a monovalent or divalent cation. In the case of a trivalent cation, however, the discharging effect of that ion comes immediately to the fore.

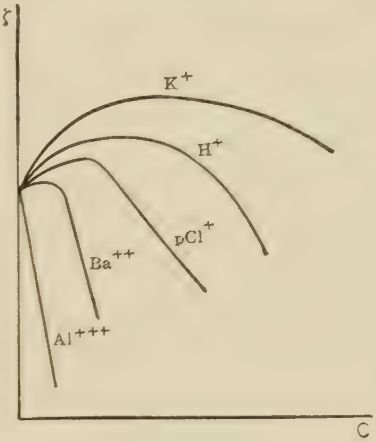

Fig. 40.

Whereas the preceding statements hold for concentrations below 100 μ-moles (1 μ-mole = 10^{-6} mole), we find that for larger concentrations the lowering of the potential by cations is accentuated. The smallest decrease is caused by a common inorganic cation of a light metal like K, followed by the hydrogen ion, while a still stronger action is exerted by an organic ion, viz., *p*-chloraniline indicated by p Cl^+ in Fig. 40. Then comes the divalent cation Ba, and finally the trivalent cation Al which lowers the charge to zero at the low concentration of 0.8 μ-mole. Apart from this decreasing effect of polyvalent cations, we may infer from these investigations that small concentrations of an electrolyte raise the boundary charge with respect to pure water, while greater concentrations lower it.

The researches of Powis,[3] carried out at practically the same time as the preceding experiments, led to the same result. Powis calculated the boundary potential both at the oil-water interface and at the glass-water interface (*cf.* p. 61, from the measurements of the cataphoretic velocity of oil drops. The equation (5) used by Powis should be corrected (Debye) as stated on page 84.

Figure 41 reproduces his data graphically. Here again we find that the potential ζ is raised for small concentrations, especially for a polyvalent anion; for instance, the tetravalent anion of $K_4Fe(CN)_6$ increases the potential strongly, as does the chlorine ion in KCl. The fact that the elevation by $BaCl_2$ is not visible is probably due to the absence of measurements at concentrations smaller than 200 μ-moles.

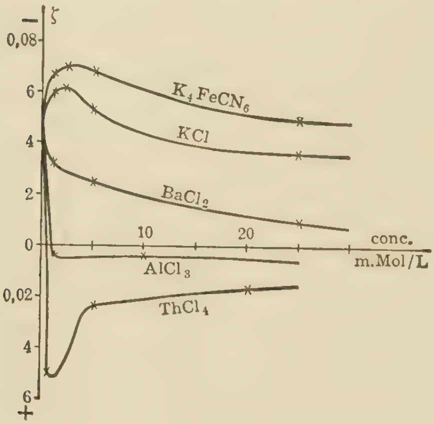

FIG. 41.

28. Significance for Colloid Chemistry. — In the previous chapter we saw that a colloid is stable only when the electric potential difference at the boundary is higher than the critical potential. In Sec. 27 it was found that the boundary potential for pure water is, generally speaking, not high, but is raised by very small quantities of electrolyte.

Figure 42 gives an idea of the change in boundary charge, ζ, with the concentration of electrolyte. The critical potential is indicated by the broken line.

The figure shows that a colloid, in order to be stable, usually requires a small concentration of electrolyte (point *a*), while an excess of electrolyte (point *b*) destroys the stability. (It should be remembered, however, in connection with this figure, that peptizing and flocculating electrolytes are, as a rule, not the same.)

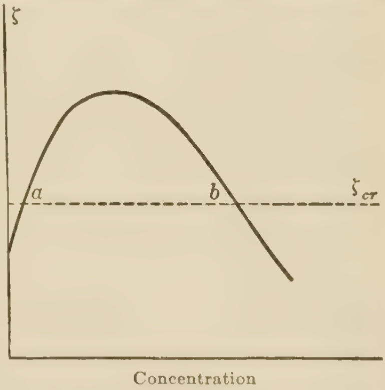

FIG. 42.

The necessity of having traces of an electrolyte for stabilizing a sol has been known for a long time. In general, we speak of peptization when matter is brought into colloidal solution and the substances which are *added* for this purpose are called: peptizing agents, or briefly: peptizers. It will be clear in this connection that a stable colloid always contains traces of electrolyte as a peptizing agent. Usually these traces are present from the preparation of the sol. If one should try to remove them purposely by excessive dialyzing, it could only be done at the expense of the stability. Graham,[4] and later A. W. Thomas and A. Frieden,[5] found, for instance, that excessive dialysis of ferric oxide causes the sol to flocculate in the dialyzer. Kruyt and van der Willigen [6] observed that even diluting with water is sometimes sufficient to bring about flocculation as, for instance, in the case of the positively charged AgI (peptized by $AgNO_3$). Beans and Eastlack [7] stated that in preparing gold sols electrically the presence of traces of electrolyte is necessary.

Ellis,[8] in his experiments, found that the OH ion raises the maximum in the potential curve to a considerable extent. Powis [8] showed that a polyvalent ion likewise gives rise to a pronounced maximum. The more the anions, either by their high valence or by strong adsorbability, increase the negative charge, the better peptizers they are. The same is true for cations with respect to positive colloids. Iron oxide is readily peptized by $FeCl_3$. In general, the salts of polyvalent metals and the hydrogen ion in acids are suitable peptizers for positive colloids. The researches of Heinz and Franz (see p. 105) furnish a beautiful illustration of the peptizing action of electrolytes. A SnO_2 sol can be prepared by peptizing precipitated tin oxide with alkali. In the making of this sol, there is an increase in the ratio between alkali and tin oxide, and a consequent increase in the cataphoretic velocity, and hence in the charge.

With reference to the point *b* in Fig. 42 it is evident that this point relates to the flocculation concentration and Powis' study of the critical potential dealt, therefore, with this point. More recent investigations have taught, however, that an apparently simple behavior as Powis found for oil emulsions does not hold in general. The theory of Powis may be expressed by the following diagram (Fig. 43). The point *A* indicates the potential of the sol containing the peptizing electrolyte. The curves I, II and III represent the values of ζ (computed from the cataphoretic velocity) as a function of the concentration for mono-, di- and trivalent ions, respectively. According to Powis then, the points b_1, b_2 and b_3 on the horizontal line of the critical potential (ζ_{cr}) indicate the flocculation concentrations. Freundlich and Zeh [9] and, later, Kruyt and van der Willigen [10] found, however, that the slope of curve I is not as represented in Fig. 43. Powis [11] had already observed that in the case of the As_2S_3 sol the shape of the curve was different from that drawn in the figure. Kruyt and van der Willigen ascribed this anomaly to the fact that the calculation of ζ from u did not take into account the variation in D. Since the values of D (as yet undetermined), for such comparatively high concentrations of electrolyte as are required for flocculation with KCl, etc., greatly exceed the value of D for pure water,[12] it is obvious that this method of computation is not permissible, as was pointed out on page 84. Although it would seem, therefore, that the theory fails for monovalent ions, Kruyt and Briggs [13] were able to show that it does apply perfectly well when monovalent ions of great flocculating power, such as strychnine or new fuchsin are employed. In that case, high electrolyte concentrations and the resulting complications with respect to D are avoided. The last named research again strongly confirms the whole concept of Hardy–Powis.

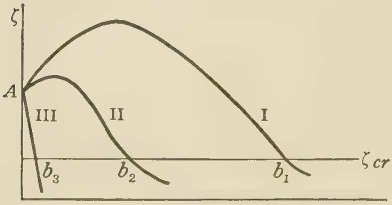

Fig. 43.

The action of peptizers will be discussed later (Chap. VI).

29. Summary.—The content of the two previous chapters may be summed up graphically in Fig. 44. In the upper part of the figure is sketched the change in the boundary charge with the concentration of the electrolyte (*cf.* Fig. 40). The broken line gives the value of the critical potential, ζ_{cr}, for the sol (*cf.* Fig. 42). In the lower half of the picture is drawn the adsorption isotherm for the electrolytes KCl, $BaCl_2$, and $AlCl_3$. Since this part of the figure is drawn to the same scale of abscissae, the ordinate representing the amount adsorbed is plotted downward. The lower part is nothing but Fig. 35 upside down. In both illustrations the same idea is expressed in two ways. In the upper half are found the concentrations at which the potential is lowered to the critical value, while in the lower half are found the concentrations at which so much cation is adsorbed that the lowering is brought about. Hence, the corresponding values must lie at equal equilibrium concentrations. Figure 44 thus unites in a single illustration the whole content of the foregoing chapters. It must be understood, of course, that the same reservation applies as was made on pages 62 and 72 with regard to the lower part of the figure. (Cf. page 97.)

30. Irregular Series.—In Sec. 28 the line for $AlCl_3$ was continued only to the point where the charge was reduced to zero.

On page 58 it was stated that further additions of salt reverse the charge, with the result that the wall acquires a positive charge; but in the long run the chlorine ion depresses this positive charge and a second discharge takes place.

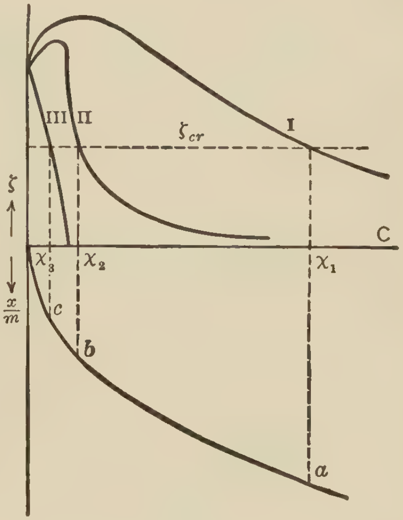

Fig. 44.

The phenomena observed when a sol is flocculated by means of an electrolyte such as $AlCl_3$ agree well with the changes in boundary potential. When increasing amounts of $AlCl_3$ are added to a negatively charged sol of mastic,[14] we notice that small concentrations cause flocculation, somewhat higher concentrations produce another stable sol of opposite sign, i.e., positively charged, while still higher concentrations bring about another flocculation. This is represented schematically in the upper part of Fig. 45 where the amount flocculated is plotted as ordinate against the salt concentration as abscissa while the lower part indicates the course of ζ as a function of the concentration.

We have, therefore, first a non-flocculation zone; but as soon as the negative critical potential is reached, flocculation begins. This primary flocculation zone ends when, after reversal of the charge, the positive critical potential is attained. From that concentration on, the $AlCl_3$, instead of causing flocculation exerts a re-charging action. Hence the mastic sol is positively charged in this second zone of non-flocculation. But, positive boundary layers are discharged by anions and the positive potential, after going through a maximum value, is reduced by the Cl ions until the critical potential is reached. At that point, a second flocculation zone begins.

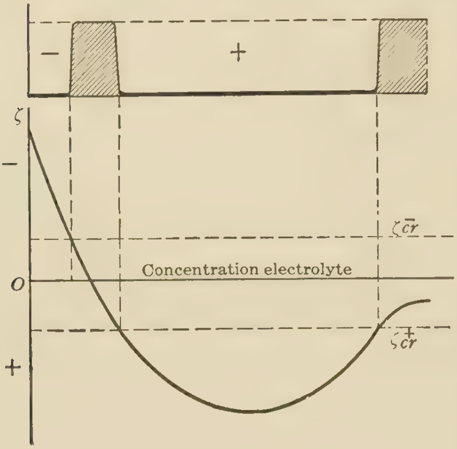

Fig. 45.

This phenomenon is designated as an *irregular series.* It will always occur when the potential-lowering effect of the cation is far in excess of the potential-raising effect of the anion. This lowering effect may be due either to a high valence of the ion or to a high degree of adsorbability. Polyvalent cations give, therefore, irregular series when they are combined with monovalent anions. But monovalent *organic* cations act in the same way. For instance, strychnine nitrate,[15] as well as new fuchsin, yields an irregular series with As_2S_3 sol, and $AgNO_3$ with the sol of HgS,[16] because in each case the cation is strongly adsorbed.

A converse reasoning applies to positively charged sols. Here the anion discharges, while the cation may raise the charge. Whenever there is a great contrast between the two ions, an irregular series will occur; hence, we readily understand why the positively charged sol of iron oxide forms an irregular series with sodium phosphate (monovalent cation *vs.* trivalent anion), and with NaOH (monovalent ions, but anion strongly adsorbable).[17]

31. Influence of Sols on Each Other.—(*a*) *Mutual flocculation.*—When a positively charged sol and one that is negatively charged are brought together, the probability of adhesion is naturally quite high, since the charges, being opposite in character, promote adhesion. In case a *small* quantity of a positively charged sol is added to a negatively charged sol, a certain number of particle adhesions will no doubt take place, but the critical potential for the combined particles will not be reached. Only when a sufficient quantity of the oppositely charged sol is added does complete flocculation occur. The same reasoning applies to a positively charged sol to which a negative sol is added. Figure 46 expresses the facts as stated here. The coördinates are the same as in Fig. 45. The very first addition of the sol of opposite sign lowers the charge; but as long as the critical potential is not reached, there is merely a decrease in stability without visible flocculation. A zone of flocculation exists only in the center, as indicated by the cross-hatched part of the figure.

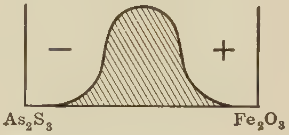

Fig. 46.

(*b*) *Protective action.*—When a sol of gelatin, for instance, is added to a gold sol prepared by the reduction of a gold salt in an alkaline medium, it appears that the gold sol is strongly protected against the flocculating action of electrolytes.

We shall find in Chapter XIII that emulsoid sols are, to a great extent, unaffected by the presence of electrolytes. Obviously the particles of the emulsoid sol are adsorbed by the gold and impart their properties largely to the gold particles.

Conversely, this protective action is used to distinguish between different emulsoid sols. The gold-number is defined by Zsigmondy [18] as the weight, in milligrams, of the dry material in the emulsoid sol which is just sufficient to prevent the change from red to blue in 10 cc. of a gold sol, after the addition of 1 cc. of a 10 per cent solution of sodium chloride. Table XIII gives the

TABLE XIII

Gold-numbers (Protective Action)

Colloid	Gold-number	Reciprocal gold-number
Gelatin...........	0.005–0.010	200–100
Casein...........	0.01	100
Gum arabic.......	0.15–0.25	7–4
Tragacanth.......	2	0.5
Dextrin..........	15	0.07
Starch...........	25	0.04
Silicic acid sol.....	∞	0

gold-numbers for a number of emulsoid sols. In the last column is found the so-called reciprocal gold-number, which is, therefore, a measure of the protective action.

(*c*) *U-number.*—When a protein sol is added to an acid gold sol, no protective action takes place. On the contrary, the gold sol is flocculated by minute quantities of the emulsoid. These so-called U-numbers ("*Umschlagszahlen,*" according to Zsigmondy) [19] represent the number of milligrams required to produce the color changes in 10 cc. of the gold sol. A few examples are given in Table XIV.

TABLE XIV

U-numbers

Colloid	U-number
Glycocoll.......	>80
Hystidin.......	0.1 –0.2
Pepton.........	0.04 –0.06
Gelatin.........	0.002–0.004
Albumose......	0.002–0.004
Casein.........	0.002–0.004

In Chapter XIV we shall see that emulsoid sols (albumen at least) change their charge under the influence of the hydrogen-ion concentration of the medium; i.e., they become positively charged in an acid solution and negatively charged in a basic solution. In the case of protective action, both the gold sol and the gelatin are negatively charged. In dealing with U-numbers, we bring together in an acid medium a negative gold sol and a positively charged gelatin sol. The result is, therefore, mutual flocculation, when both colloids are present in the proper quantitative proportions. An excess of the positively charged protein sol, leads, of course, in accordance with Fig. 46, to a positively charged protein-gold aggregate sol.

(*d*) *Sensitizing.*—Experiments by Brossa and Freundlich [21] have indicated that a decrease in the stability of suspensoids is often noticed on the addition of an emulsoid of opposite charge. On adding to the positively charged sol of Fe_2O_3 a solution of albumin, carefully freed from electrolytes and carrying a negative charge, we notice that the particles unite. At the same time the charge of the iron oxide sol is lowered, although it retains its stability. However, the amount of electrolyte necessary to precipitate the sol, viz., the flocculation value, appears to have decreased enormously. Accordingly, we might say that the added albumin has a sensitizing effect on the iron oxide sol. In a sense, we have already met with a certain kind of sensitization when discussing Fig. 46. In fact, in the non-cross-hatched parts of the figure, there is a gradual lowering of the charge on the addition of the sol of opposite charge. U-numbers also belong in this category.

It is likewise possible that suspensoids sensitize each other. On mixing a negatively charged sulphur sol with an As_2S_3 sol, also having a negative charge, we find that they sensitize each other. The reason for this behavior is, however, a special one. The peptizing electrolyte (see p. 108) for the sulphur sol appears to be pentathionic acid, while hydrogen sulphide peptizes the As_2S_3 sol (see p. 76). These two peptizing compounds react with each other, according to the following equation:

$$H_2S_5O_6 + 5H_2S = 10S + 6H_2O,$$

and, as a result, the boundary layers of the particles are disturbed and the charge lowered.[22] Only in a special case like this do sols of the same charge exert a sensitizing effect on each other. In general they do not influence each other.

(*e*) *Earlier conception of irregular series.*—Formerly the opinion prevailed that the irregular series required a different explanation from that given in Sec. 30. When $AlCl_3$ is added to a dilute solution of mastic, it might be supposed that a sol of Al_2O_3 would be formed by hydrolysis, and that, first of all, a mutual flocculation would take place, as discussed in Sec. 31*a* with a reversal of the charge from negative to positive. In the long run, the chlorine ion might finally bring about flocculation of this mastic complex.

A serious drawback to this explanation is the fact, already mentioned, that sodium hydroxide gives an irregular series with Fe_2O_3 sol. Moreover, it is possible to modify one and the same system in such a way that the normal picture of the irregular series can be clearly distinguished from the phenomenon of mutual flocculation.

For instance, on treating a neutral gold sol with $Th(NO_3)_4$, an irregular series is formed. But we can also study the process by using an alkaline sol, in which case the alkali really hydrolyzes the $Th(NO_3)_4$.[23] Table XV gives the values for both series.

These data show strikingly the contrast between precipitation by the Th ion, which requires only a minute quantity, and flocculation by the colloidal ThO_2, which necessitates a much larger amount because the Th ion is active electrically only insofar as it is present in the double layer of the ThO_2 particles. In the case of the ion-dispersed solution, each individual Th ion is, of course, active. Furthermore, a great difference is noticeable, viz., the neutral sol shows a normal color change from red to blue, while in the alkaline series the gold precipitates in the form of red flakes. Such red flakes always occur when a gold sol is precipitated by a sol of opposite charge. For instance, the precipitate from a gold sol plus a tin oxide sol is known under the name of "purple of Cassius"[24] and an analogue of this is formed when gold and thorium oxide interact. Table XVI shows that red flakes are obtained indeed on mixing a gold sol and a sol of ThO_2.

TABLE XV

Gold Sols + a Solution of $Th(NO_3)_4$

	Conc. in millimoles per liter	
	Neutral sol	Alkaline sol
1st flocculation value	0.00090	0.03
End of 1st flocculation zone	0.0030	ca. 0.10
2nd flocculation value	20	ca. 5

TABLE XVI

Alkaline Au Sol + ThO_2 Sol

Conc. ThO_2 in millimoles per liter	Condition after 5 min.
0.002–0.10	red sol
0.25 –0.50	red flakes
0.60 –7	red sol

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CHAPTER VI

CONSTITUTION OF THE DOUBLE LAYER

32. The Double Layer.—The conception that colloidal particles are electrically charged is likely to lead to the erroneous idea that each of these particles carries an electric charge and hence that a sol can be represented as an aggregate of statically charged electric spheres.

Von Smoluchowski[1] has rightly countered this conception with the remark that if it were correct an electroscope would show a deflection when brought close to a sol. Since this is not the case, the electric charges must be self-compensating, a fact which finds a proper expression in Helmholtz' well-known idea of an electric double layer. Opposite the ions that give to a particle, say, a negative charge, there are located positively charged ions with the same total electric charge (see Sec. 18). As a result of this, the system as a whole appears to be uncharged; hence, the phenomena of motion, discussed in Chapter III, take place whenever there is displacement in the electric double layer, caused by the existence of a certain amount of slip between the two coatings of this double layer. Under the influence of an electric potential, these coatings move in opposite directions, tending to set up an opposing electromotive force. They do not do so, however, for the reason that the electrical conductance of the liquid causes an exchange; hence, the following conditions, represented schematically in Fig. 47, occur successively.

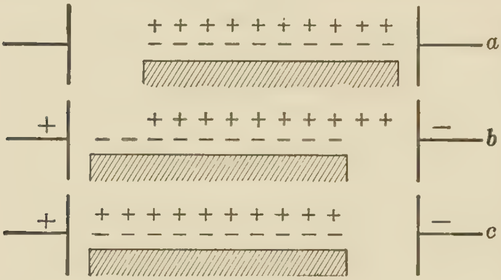

Fig. 47.

Imagine a particle (indicated in cross section by the shaded area in Fig. 47*a*) placed between two electrodes. When an electromotive force is applied, the two coatings are displaced and the particle moves along with the negative charge (Fig. 47*b*). This leaves electric charges free on either side. These are compensated, however, by the intermicellar liquid (a solution of a peptizing electrolyte and hence a conductor of electricity). The condition of Fig. 47*c* is thus established. The net result, therefore, is that the whole particle plus its double layer has moved toward the positive electrode. Simultaneously, something else, to which we shall refer in the next sections, has migrated in the opposite direction.

The conception of an electric double layer, introduced by HELMHOLTZ,[2] is based on the supposition that the oppositely charged layers are at a molecular distance from each other. This is represented schematically in part I of Fig. 48 where the cross-hatched area indicates the solid wall (of a cataphoretic particle or a capillary) to which adhere, as we assume in the figure, negative ions. The dotted area containing these anions is, therefore, that part of the double layer which sticks to the

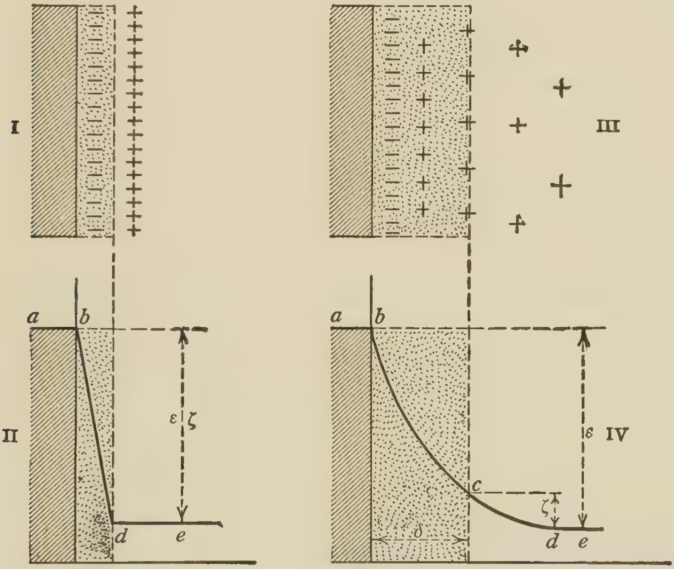

FIG. 48.

solid wall. Immediately opposite these, in the mobile liquid part of the double layer, we find an equivalent amount of cations. Figure 48, II expresses the same idea in a somewhat different manner by means of a graph with the electric potential as ordinate and the distance from the wall as abscissa. The level *ab* is the potential of the solid wall and *de* that of the liquid. The drop in potential, therefore, takes place exclusively in the layer next to the wall. Hence the curve *bd* shows a steep slope.

Gouy [3] has pointed out that this method of representation cannot possibly be correct. Although it is true that the positive ions are atrracted by electrostatic forces to the negative ions on the wall they are, nevertheless, subject to a disorderly dispersion on account of the heat motion in the liquid. These two tendencies give rise to a distribution of these cations according to a so-called *e* function of Boltzmann, viz., in a manner similar to that of the distribution of atmospheric air on the earth. There too, the gravitational attraction opposes the diffusion tendency, resulting in an atmosphere of diminishing density. (*Cf.* p. 152.) The so-called *diffuse double layer* or *ionic atmosphere* is illustrated schematically by part III of Fig. 48. Part IV of the same figure shows the corresponding shape of the potential curve: *ab* and *de* are, of course, at the same levels as before but the course between *b* and *d* showing the actual drop in potential is much more gradual.

Freundlich and Rona,[4] and later Gyemant [5] developed the idea that only a part of the diffuse double layer is mobile while the other part (the dotted area) adheres to the wall. The facts which led to this trend of thought were the following. The potential drop between glass and water (or between glass and an aqueous solution) had been measured by Haber and Klemensiewicz,[6] by means of the apparatus sketched in Fig. 49. *A* is a thin-walled glass vessel containing any liquid that is a good conductor; in this is placed an electrode, *E*. Both *A* and a calomel electrode, *CE*, dip into the liquid *B*. The latter thus contains a *glass electrode* and a normal electrode. The investigators named above measured the potential of this cell as a function of the composition of the liquid *B* and were thus enabled to calculate the potential gradient at the glass electrode. Kruyt,[7] in his investigations on flow potentials, also measured potentials for the glass-water boundary, or glass-electrolyte solution. Powis,[8] too, calculated such potentials from his measurements of electro-endosmotic movement in the neighborhood of a glass wall. Whereas, in the measurements of the two last-named authors, the great effect of the valence of the oppositely charged ion came to the fore, the measurements of Haber and Klemensiewicz showed that the potential of the glass electrode is completely unaffected by this valence. The glass electrode behaves like a hydrogen electrode and consequently changes its potential according to the well-known formula of Nernst, being dependent only on the hydrogen-ion concentration of the liquid *B*. Following Freundlich and Rona, we must, then, distinguish between two kinds of potential at the glass-liquid interface.

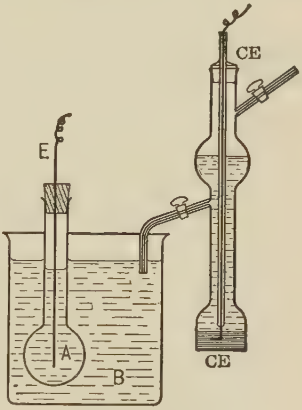

Fig. 49.

Figure 48, IV, explains the situation clearly. What Haber and Klemensiewicz measured is the total potential difference between the wall and the liquid, viz., the difference in level between *ab* and *de*, expressed by ϵ in the figure. In electro-capillary experiments such as those of Kruyt and those of Powis the active potential difference is that which exists between the wall and the liquid that moves alongside. Since, however, there is liquid adsorbed on the wall the point *c*, under these circumstances, represents the potential at the wall. Hence the potential difference measured in capillary electric processes is only the part ζ in the figure. For this reason ϵ is called the *transverse* and ζ the *tangential* potential difference, ϵ being the potential difference that plays a rôle in the thermodynamic considerations leading to the well-known formula of Nernst, while ζ is the potential difference, mentioned in our discussions in Sec. 24, which refers to the movement of the liquid and the wall with respect to each other. Hence the terms *thermodynamic* and *electrokinetic* potential also refer to ϵ and ζ, respectively.

Figure 48, IV, is of paramount importance in colloid chemistry for we know that colloid stability runs parallel with the potential drop of capillary electric processes, that is to say, with ζ. Text-books of electrochemistry inform us about ϵ, the total potential difference which does not take in account the course of the potential curve in the boundary layer, and hence ϵ can teach us nothing about colloid chemistry. We must, therefore, study the character of the ζ potential.

We notice at once that the location of c which determines completely the magnitude of ζ, depends, in the first place, on the shape of the potential curve bd and, secondly, on the thickness of the adhering layer δ.

The shape of the potential curve has been discussed by Gouy who finds that the course of the curve is a function of the concentration of the electrolyte and of the valence of the ions in the solution. In case the liquid is approximately pure water, the ionic atmosphere stretches out very far and gives rise to a very gradual drop in potential. In other words, the curve bd is only slightly inclined. An *increase* in the electrolyte concentration, however, would force the potential curve back into the dotted area and bring about a reduction of ζ (during which change ϵ may remain absolutely the same as before!). For various reasons, the theory of Gouy is, however, incomplete. For instance, while the valence is taken into consideration, no mention is made of the adsorbability of the ions and it is precisely this specific property which is of the greatest significance for capillary electric processes and the phenomenon of flocculation. Stern[9] has tried to introduce this factor into the discussion but his theory contains too many simplifying assumptions. In spite of these, the net result is too complicated to serve as a basis for a quantitative test. For a general orientation, however, the line of reasoning developed by Gouy and by Stern is of considerable importance.

Very little is known with regard to the thickness of the adhering layer. It should always be remembered that we are not at all certain that δ remains constant when conditions are changed, for instance, by a variation in the electrolyte concentration. Furthermore, in the derivation in Sec. 24 the quantity δ was introduced twice but each time in a different sense: once, in the computation of the drop in velocity caused by friction, and, again, as the distance between the coatings of the double layer. In the final expression, the two δ's cancel. It is evident that the identity of these δ's which is at best doubtful in the case of a Helmholtz double layer, certainly does not exist for a diffuse double layer. A new element of uncertainty enters, therefore, into the calculation of ζ from cataphoretic velocity (see also p. 88).

In Sec. 18 we pointed out that a distinction must be made between the " charge of the particle " and the " potential of the double layer "; these are quantities which are related to each other by the condenser formula. In the case of a HELMHOLTZ double layer, the interrelation is simple and readily understood because $\epsilon = \zeta$, but the introduction of a diffuse double layer leads to a variety of questions. It is perfectly obvious that a simple proportionality between e and ζ no longer exists since part of the charge no longer contributes to the potential difference ζ. If, moreover, δ is variable, one and the same charge on the solid wall may result in a great variety of ζ values.

Now that the concept of the HELMHOLTZ double layer has been abandoned as inadequate, one might gain the impression that the discussions in the preceding chapters dealing with the *charge of the particles* have become meaningless since it is in reality the potential difference in the double layer which determines the stability of colloids. The situation is, however, not hopeless provided we take properly into account the conditions expressed in Fig. 48, IV. Let us assume that there is, per unit area of the solid particle, a charge $-e$ (the minus sign designates a negative charge). The total atmosphere of the diffuse double layer, insofar as the latter occupies a cylinder with a base of unit area cross section must contain a charge $+e$. This charge is divided in two parts, viz., e_{bc} located inside the liquid that adheres tightly to the wall and e_{cd} which is found in the movable part of the liquid. The potential ζ is then due to a double layer consisting of a negative charge $- e + e_{bc}$ and a positive charge e_{cd} which are numerically equal. If we imagine that the positive charges of the movable part of the liquid (see Fig. 48, III) are concentrated in an electro-gravitational plane, the thickness δ of the double layer which is effective for ζ, is represented by the distance between the gravitational plane and the point c. We find, therefore, that ζ is still the potential difference of a double layer, but not of the one that we had in mind originally. This difference, however, is replete with consequences for our considerations. The active charge in the double layer is no longer the total charge $-e$, but only a part of that, viz., $-(e - e_{bc})$. Hence, we understand at once why FREUNDLICH's theory of flocculation has proved to be incorrect in general. As we know, this theory is based on the idea that the charge per unit area of the particle (e_o, giving rise to a transverse potential ϵ_0 and a tangential potential ζ_o) has to be lowered by a certain charge of opposite sign furnishing an equivalent amount of oppositely charged ions in order to reach the critical values e_{cr}, ϵ_{cr} and ζ_{cr}. Now the relation between e and ϵ is simple, but not that between e and ζ. The latter, as we saw, is the factor that governs the stability of colloids. There is a critical ζ potential which is, for different electrolytes, not at all connected with a definite critical electric charge. Both the shape of the potential curve and (possibly) the thickness of the adhering layer may differ from one electrolyte to another.

Only in case the double layer approaches the character of a Helmholtz layer, does the rule of equivalences apply; the total value of e then determines ζ, which is, to be sure, identical with ϵ.

Recapitulating, we may state that the *charge* of the colloid particle, as mentioned in previous chapters, is not the total charge e but only $e - e_c$. The particle must be considered as being bounded not by its solid surface but by the superficially adhering layer of liquid. In discussing stability we have to consider only the double layer formed in the movable liquid and the potential difference of this layer is given by the all-controlling quantity ζ.

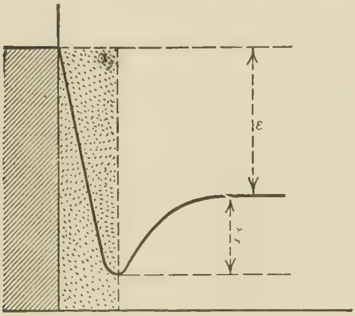

Fig. 50.

The course of the potential curve is probably not always so simple as would appear from Fig. 48, IV; in fact, we know (*cf.* p. 58) that the sign of the ζ potentials is sometimes reversed by neutral electrolytes. Figure 50, which shows a ζ potential with a sign opposite to that of ϵ, takes this possibility into account.[9*]

33. The Constituents of the Double Layer.—Meanwhile, it is very important to know which ions really constitute the electric double layer. About twenty years ago, the view adopted was that a neutral wall in contact with water took on a *negative* charge since it had a preference for adsorbing the hydroxyl ions of water. A wall made of material having a decidedly basic character, such as Al_2O_3, which we know has a positive charge, was supposed to have a special affinity for the hydrogen ions of water; hence, Al_2O_3 became positively charged. In case the material of the wall had a decidedly acid character, the specific preference for hydroxyl ions was explained in a similar manner.

Freundlich and Elissafoff [10] suggested in 1912 that the material of the wall, insofar as it can be considered to be an ionogen, might participate in the formation of the double layer. The question that arises, then, is whether this hypothesis should not be generalized by assuming the lining of the double layer to be built up, in all cases, from the ions of the material of the wall. This is, of course, quite possible in the case of ionogens such as glass (silicates), metallic oxides, salts, and the like. We get into difficulties, however, with substances like naphthalene. Some recently developed ideas of Langmuir and Harkins (*cf.* p. 48), in which the double bond in the benzene nucleus is supposed to be the special carrier of capillary electrical properties, might possibly lead to a reconciliation.

It is obviously extremely difficult to determine the constituents of the double layer directly, but there are, nevertheless, various indications which give us a better insight into the constitution of the double layer of colloidal particles.

There are two remarks that should be made before these experiments are discussed. In the first place, one might ask, speaking of the sols of metals, whether the electric double layer here is not simply the one that plays a part in Nernst's so-called osmotic theory of solution tension. The double layer would then be formed by the metal ions going into solution. If a potential gradient were produced in this manner, the electromotive series would play an important rôle in the order of the capillary electrical phenomena, which is not at all the case. Furthermore, colloids of noble metals, such as those of gold or platinum should be positively charged, whereas we know that these sols are negative. It is, however, easy to collect arguments showing that the double layer of a silver particle, for instance, does not consist exclusively of silver ion sent into solution by the silver. As a matter of fact, OH ions favor the formation of negative metallic sols, but ammonia is very harmful to the preparation of a silver sol. Since silver oxide is soluble in ammonia, we cannot get away from the impression that silver oxide or some other complex of Ag plays a part in the double layer of a silver sol. Reference will be made to this in a later section.

Furthermore, the preceding discussion has indicated that the potential gradient resulting from a solution tension might be a measure of ϵ, but surely not of ζ.

For non-conductors of electricity we might conceive of a special kind of mechanism imparting an electric charge to the particles. COEHN,[11] for instance, noticed that non-conductors of electricity, brought into contact with each other, produce a condition whereby the substance with the higher dielectric constant is charged positively with respect to the one having a lower constant. This rule, however, can be of little aid in the explanation of the electrical properties of colloids, since it does not appear that an intimate relation exists between flocculation phenomena and variations in the dielectric constant. As is well-known, water has an exceedingly high dielectric constant (81). Substances with a lower dielectric constant, viz., practically all sols hitherto studied, should, therefore, be negatively charged in water. The effect of traces of an electrolyte on the dielectric constant of water and, likewise, their effect on capillary electrical processes and on the stability of sols, does not support the idea that the dielectric constant is a determining factor. Then, too, COEHN's rule does not apply to tangential potential differences but only to transverse ones.

34. The Tin Oxide Sol.—Considerable information concerning the constitution of the double layer may be obtained from certain investigations on the sol of tin oxide, carried out in the laboratory of ZSIGMONDY.[12]

When $SnCl_4$ is poured into water, a gelatinous precipitate of SnO_2 is formed and settles slowly. The HCl simultaneously formed is removed by decanting the supernatant liquid repeatedly. The SnO_2, thus purified, is brought into colloidal solution by adding either an acid or a base to the precipitate of SnO_2. Addition of KOH produces a negative SnO_2 sol, while with HCl we obtain a positively charged sol.

According to the old conception mentioned above (*cf.* p. 102), we might say that the particle adsorbs either H ions or OH ions preferably, builds up the lining of the double layer with these ions, and derives its charge from them.

We shall not discuss here the experiments of MECKLENBURG[13] on the influence of the previous treatment of the precipitate on the properties of the sol, interesting as they are, but shall confine ourselves for the present to the investigations of Heinz and Franz on the flocculation value of the negatively charged tin oxide peptized with alkali.

A number of sols were prepared for which the ratio of SnO_2 to KOH was different. At the top of Table XVII is indicated the ratio *N* in gram-moles for each sol. For each of the salts mentioned in the first column, the table gives the flocculation values. Looking over these values, we notice that the monovalent cations, which give approximately the same value, form one group, while all other salts, yielding a different value, which, however, is practically the same for all of them, form another group. This latter circumstance is very striking when we take into account the fact that this second group contains the monovalent H and Ag ions, the divalent Ca and Ba ions, and the trivalent Al ion. We expect, indeed, to find that all these ions have a smaller flocculation value than the monovalent ions, but from the point of view developed on page 71 it is difficult to see why all these ions should show flocculation values which lie so close together. Still more remarkable is the fact that this figure for the flocculation value reappears in the last line of Table XVII, where the amount

TABLE XVII

Flocculation Value, SnO_2 Sol, in Milli-equivalents per 10 cc.

$N=\frac{SnO_2}{KOH}$	2	10	25	50	100
NaCl	1.8	1.7	0.34	0.26	0.14
$NaNO_3$	1.9	1.5	0.30	0.28	0.14
Na_2SO_4	1.8	1.7	0.32	0.28	0.14
NaH citrate	2.3	2	0.40	0.52	0.50
HCl	0.33	0.07	0.025	0.0135	0.007
$CaCl_2$	0.33	0.075	0.022	0.0135	0.007
$BaCl_2$	0.35	0.065	0.022	0.0130	0.007
$AlCl_3$	0.33	0.07	0.025	0.0135	0.007
$Al(NO_3)_3$	0.33	0.075	0.024	0.0140	0.007
$AgNO_3$	....	....	0.025	0.0180	0.009
Alkali in 10 cc.	0.333	0.065	0.026	0.013	0.0064

of alkali present in each sol is shown. This leads, therefore, to the inference that all ions mentioned in the second part of the table give a flocculation value which is exactly equal to the amount of alkali used for peptization.

From these data, Zsigmondy [14] has drawn a very acceptable conclusion regarding the constitution of the double layer of the SnO_2 particle. Assuming that peptization does not take place by the mere adsorption of OH ions but that the added KOH reacts chemically with the outside molecules of the colloidal particle, we arrive at a picture of the particle plus its double layer, as represented in Fig. 47. Zsigmondy's assumption is, therefore, that the stannates formed at the boundary of the particle produce the ions of the double layer. Considering, furthermore, that the ions in the upper part of the table give soluble stannates, and those in the lower part form *insoluble* stannates, we realize that a particle is precipitated when the boundary layer is destroyed because the potassium stannate, which forms the double layer, is changed into an insoluble stannate. (In the case of HCl, stannic acid itself, which is also insoluble in water, is formed.)

The idea that the lining of the double layer is made up not of OH ions but of SnO_3 ions is rendered very plausible by these investigations. In addition, we find that a double layer can be destroyed in a manner differing from that discussed on page 71; we cannot, however, discard the previous explanation, since either one mechanism or the other may produce the effect. In fact, even for the SnO_2, the formation of an insoluble substance in the boundary layer can serve only as a working hypothesis for the electrolytes of the second half of Table XVII. For those of the first half we are undoubtedly dealing with the mechanism previously discussed, in which the adsorption of the oppositely charged ion plays the principal part.

35. Analogous Cases.—In Sec. 34 we saw that the double layer of a tin oxide particle is formed by a constituent related to the substance from which the particle is made: the stannates take a polar position when attached to the related material. In a sense this behavior is in line with the theory of Langmuir and Harkins, which postulates that the molecules of the boundary layer always tend to make the transition of the phases gradual: The stannates turn their stannic acid anion toward the tin oxide. When peptization by HCl takes place, the double layer is probably made up of molecules of $SnCl_4$ pointing their cation toward the (thus negatively charged) tin oxide particle. Zsigmondy[15] has introduced a simple and ingenious method of representing the constitution of a sol: without taking into account the possibility of hydration, he writes the composition of the particle down in a rectangle and adds the ion that forms the lining of the double layer. We thus obtain, for the negative SnO_2 sol, $\boxed{SnO_2}\,SnO_3^{--}$; and for the positive SnO_2 sol, $\boxed{SnO_2}\,Sn^{++++}$.

This special location of molecules that are related to the material of which the particle consists, is quite frequently met in colloid chemistry. Marck[16] has found that the MnO_2 sol can be precipitated by potassium regardless of the anion with which it is combined. An exception must be made for $KMnO_4$, which is unable, even in the highest concentrations, to precipitate MnO_2. Obviously, the permanganate ion, which is related to the material of the MnO_2 particle, has such a pronounced charging effect that the K ion cannot overcome this influence.

The positive sol of ferric oxide is usually made by hydrolyzing $FeCl_3$ and removing the HCl by dialysis. Earlier in this book (p. 87) it was pointed out that it is impossible to remove the Cl ion completely. This in itself makes it appear likely that the double layer is not formed by adsorption of hydrogen ions on the inside, and of OH ions on the outside, but that the chlorine plays a significant part.

Various investigations[17] dealing with the flocculation of the iron oxide sol have shown that all anions having a valence of two or more, and also the OH ion, give practically the same small flocculation value, as is seen from Table XVIII. Monovalent anions, on the other hand, have a much larger flocculation value (see also Table XI, p. 74; it should be noted, however, that this table refers to a much more dilute sol). This result agrees well with that obtained for tin oxide, the more so where the amount of polyvalent ion is always equivalent to the quantity of chlorine ion already present, which clearly functions as a peptizer (*cf.* p. 87). It is reasonable to assume that the double layer consists of a combination of basic iron chloride and chlorine. Zsigmondy[18] suggests the following representation, which is quite acceptable: $\boxed{Fe_2O_3}\,Fe_2O_2^{++}$. Hence, he considers that $Fe_2O_2Cl_2$ is the electrolyte which forms the double layer.

This brings up a question as to the correctness of our earlier conception regarding the nature of the double layer (see p. 76) of, say, As_2S_3. One might ask: Does not the peptizer, H_2S, furnish the material for the double layer? This in itself is not probable, since if it were true we should have to explain why, in this case, the hydrogen is not preferentially adsorbed as we have found it to be in so many other cases. Very likely we meet here again with the tendency of the boundary layer to make a gradual transition from the particle to the dispersion medium. Possibly the constituent of the double layer is sulpho-arsenious acid, $HAsS_2$, so that the particle has the following constitution:

$$\boxed{As_2S_3}\ AsS_2^-.$$

TABLE XVIII

Flocculation Value, Fe_2O_3 Sol in Milli-equivalents per Liter

Electrolyte	γ
KNO_3	188
OH	1.61
Citrate	1.65
CrO_4	1.52
CO_3	1.7
SO_4	1.7
PO_4	1.9
$Fe(CN_6)$	1.3
Chlorine contents of the sol	1.66

In the same way, the sulphur sol obtained by the reaction:

$$2H_2S + SO_2 = 3S + 2H_2O$$

is peptized by a special sulphur-containing acid which furnishes the ions for the double layer. When the above reaction takes place, there is also formed pentathionic acid, which probably builds the double layer, so that the particle of sulphur has the following constitution: $\boxed{S}\ S_5O_6^{--}$. Experiments by Freundlich and Scholz [19] have supported the probability of this assumption (see p. 93).

In recent years, considerable dispute has centered on the question of the double layer of gold sols. Zsigmondy,[20] in 1925, still considered that its formation is due to preferentially adsorbed OH ions which build up the inner coating of the double layer, while the outer coating is formed by alkali or hydrogen ions. The constitution then, would be: $\boxed{\mathrm{Au}}\,\mathrm{OH}^- + \mathrm{K}^+$. Pauli and Fuchs,[21] in extensive researches, have tried to prove that the double layer consists of ions of aurates, leading to a structure: $\boxed{\mathrm{Au}}\,\mathrm{AuO_2}^- + \mathrm{K}^+$. This is more likely not only on the basis of their experiments but precisely in connection with the cases mentioned above, viz., the close relationship between the material of the particle and the ions that make up the inner coating of the double layer. Van der Willigen,[22] moreover, has made this *gradual* transition still more plausible by postulating the existence of a thin layer of $\mathrm{Au_2O_3}$ separating the massive gold from the aurate layer. In the case of the platinum sol, Pennycuick [23] arrives at the same conclusions as Pauli. Hence its constitution is presumably: $\boxed{\mathrm{Pt}}\,\mathrm{Pt(OH)_6}^{--} + 2\mathrm{H}^+$.

In connection with the previous discussion, attention is called to the special meaning of the term "micell(e)." This word originated with Nägeli [20] who used it to designate the colloid-chemical equivalent of the molecule of a true solution. Nowadays, with our greater knowledge of the structure of colloidal particles, we can express ourselves a little more precisely by saying that the micell is the particle plus the entire double layer. For the alkaline tin oxide, it means therefore: $\left[\boxed{\mathrm{SnO_2}}\,\mathrm{SnO_3}^{--} + 2\mathrm{K}^+\right]$. Duclaux uses the word "granule" for the particle without the outside of the double layer.

36. Extension of this Line of Thought.—The conception that the double layer does not consist exclusively of outside matter, but is partly derived from materials which are already present in the particle itself and take part in the formation of the inner coating, has led to a clear understanding of a number of phenomena.

The researches of Debye and Scherrer (see p. 134) have shown that many colloid systems hold crystalline particles in dispersion. From the work of von Laue and Bragg we have obtained an idea of the structure of the space lattice of a crystal. If we apply this concept to crystalline dispersed particles, the genesis of an electric double layer becomes perfectly clear to us.

We choose as an example a sol of a silver halide which is formed according to the following method.[26]

If $AgNO_3$ and KBr are brought together in stoichiometric properties, no sol is formed, but AgBr is precipitated. If, however, silver nitrate is present in excess, because not enough KBr has been added, we obtain a sol of AgBr which is positively charged. In case KBr is present in excess, the sol is negatively charged.

According to the above-mentioned method of presentation, these two sols have the following structure:

$$\boxed{\mathrm{AgBr}}\ \mathrm{Ag}^{+} \quad \text{and} \quad \boxed{\mathrm{AgBr}}\ \mathrm{Br}^{-}$$

positive sol negative sol.

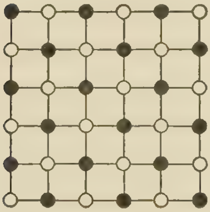

Fig. 51.

Figure 51 shows a cross section through the space lattice of silver bromide. The silver atoms are represented by ● and the bromine atoms by ○. It should be noticed that a silver atom, for instance, in the center of the space lattice, is surrounded by 6 bromine atoms, 4 in the plane of the drawing, one in front, and one behind. The affinity of a silver atom is, therefore, saturated when 6 bromine atoms are grouped symmetrically around it. This holds for all silver atoms inside the space lattice, but a silver atom on the surface of the particle is surrounded by only 5 bromine atoms, 3 in the plane of the drawing, one in front, and one behind. Hence, the crystal lattice lacks one bromine atom to saturate completely the affinity of the silver atom on the surface. Now, it is obvious that a particle of AgBr placed in a liquid containing KBr, and hence free bromine ions, will tend to add a bromine atom to the silver atom in the surface (Fig. 52). But this bromine atom is already balanced by a corresponding potassium ion. Consequently, the K ion will take its position opposite the bromine ion. This is repeated at all points of the surface where Ag atoms lie, and thus an electric double layer, consisting of bromine and potassium ions, is formed around the particle. This is indicated in Fig. 52, where ◍ represents the potassium ions.

In case silver nitrate is present in excess, thereby making silver ions available, a similar line of reasoning can be followed, since a bromine atom stands in the same relation to its surrounding 6 silver atoms as a silver atom does with regard to its 6 neighboring bromine atoms. There will then be formed a double layer consisting of silver ions all around the particle and nitrate ions on the side of the liquid. Under these circumstances, the particle is positively charged.

We may, of course, speak here of selective adsorption, provided we keep in mind that the forces causing the adsorption are characteristically the same as those that preserve the space lattice of a crystal.

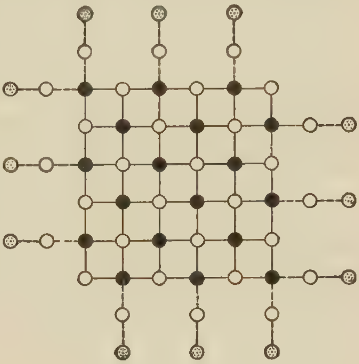
FIG. 52.

The theory regarding the double layer at the boundary of crystalline particles was first developed by MUKHERJEE[27] and was worked out independently by FAJANS.[28] It has led to the making of various other investigations concerning the condition at the surface of the particles, especially as regards the density and the distribution of the ions adsorbed on the surface.[29] KRUYT and VAN DER WILLIGEN[30] succeeded in proving that lattice forces actually play a rôle in the surface layer. Instead of adding to AgI a small excess of iodine ions, these authors also used other ions and found that only those ions which form isomorphous salts (ions that fit the lattice), give rise to the formation of a sol of AgI.

37. Peptization.—An insight into the nature of the double layer is also obtained by means of peptization phenomena. On page 86 we saw that a substance is brought into colloidal solution by the addition of an electrolyte whereby the boundary potential is raised above the critical value. A sol of HgS, for instance, is obtained by the precipitation of a solution of $HgCl_2$ with H_2S, removal of the HCl first formed by decantation and peptization of the precipitate by means of H_2S passed through the liquid. The charging effect of H_2S is apparently sufficient to stabilize the loosely cohering particles of the precipitate. As shown by VAN DFR WILLIGEN,[31] the ζ potential of this sol and its stability may be considerably increased by the addition of $K_4Fe(CN)_6$, a fact that does not surprise us in view of the strong negatively charging power of the tetravalent anion (*cf.* p. 86, Fig. 41). It might be expected, therefore, that $K_4Fe(CN)_6$ can peptize the washed precipitate of HgS. This is, however, not the case. The $Fe(CN)_6$ ion is, apparently, able to raise the potential of a double layer once formed, but cannot build the double layer. Obviously, it lacks the chemical affinity for HgS and without chemical affinity there can be no isomorphism. The H_2S, on the other hand, has the S ion in common with the HgS and always tends to form sulpho-acids. Hence this substance does form a double layer. These data clearly bring out the characteristic chemical relationship between the colloidal particle and the inner coating of the double layer.

38. Electro-valence of the Double Layer.—An important extension of our knowledge of the structure of the double layer is due to the investigations of VARGA and WINTGEN and their co-workers in ZSIGMONDY's laboratory.[32] These experiments form a valuable extension of earlier researches by DUCLAUX.

First of all, the specific conductance of the sol, κ_s, and that of the intermicellar liquid, κ_i, were determined. The intermicellar liquid was separated by the method of ultrafiltration, which will be fully discussed in chapter IX. The difference between κ_s and κ_i represents the specific conductance of the colloidal particles, κ_m. Hence:

$$\kappa_m = \kappa_s - \kappa_i. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Determinations were made on the tin oxide sol, discussed in Sec. 34, and on other sols. The cataphoretic velocity was likewise determined.

The conductance is due, on one hand, to the charged particle, and, on the other hand, to the ions in the outer mantle of the double layer. Assuming that KOHLRAUSCH's law of the independent migration of the ions applies, the equivalent conductance, λ, for the colloidal system will be:

$$\lambda = u + v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which u is the velocity of the K ion and v the velocity of the particle as we know it from the cataphoresis.

Furthermore:

$$\kappa_m = n\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n is the *equivalent* concentration of the colloidal particles, in other words, the total weight of the particles in one cubic centimeter of sol, divided by the weight of one particle times the number of electrically active unit charges per particle.

Wintgen computes what he calls the "equivalent aggregation A," i.e., the number of molecules of SnO_2 that move along with one electric unit charge (in other words, the number of gram-molecules of SnO_2 transporting 96,500 coulombs of electricity). From equations (2) and (3) it follows that:

$$A = c_{SnO_2} \times \frac{\lambda}{\kappa_m},$$

where c_{SnO_2} is the molecular concentration, i.e., the number of grams of tin oxide dissolved in one liter, divided by the molecular weight of SnO_2. Representing the ratio $\frac{SnO_2}{2KOH}$ by N, we have: A molecules of SnO_2 accompanied by $\frac{2A}{N}$ molecules of KOH (called B).

From measurements of the electrical conductivity and the cataphoretic movement, Wintgen determines, for sols with different values of N, the factor A as shown in the second column of Table XIX.

TABLE XIX

$N = \frac{SnO_2}{2KOH}$	A from el. conductivity	A from transport numbers	Structure of the micell
1	1	1	True solution: $SnO_3^{--}+2K^+$
25	65	64	$\left[\boxed{65\ SnO_2+2\ K_2O}\ SnO_3H^-\right]_{n_1}+n_1K^+$
50	160	180	$\left[\boxed{170\ SnO_2+3\ K_2O}\ SnO_3H^-\right]_{n_2}+n_2K^+$
100	600	592	$\left[\boxed{600SnO_2+5.5K_2O}\ SnO_3H^-\right]_{n_3}+n_3K^+$
200	....	1865	$\left[\boxed{1800SnO_2+9K_2O}\ SnO_3H^-\right]_{n_4}+n_4K^+$

The next step is to measure the amount of colloid transferred by the current toward the anode.

Let us review briefly the mechanism of the transport of an electric current by colloidal particles. In Fig. 47 (p. 96) this was represented schematically. Applying the result obtained (see Fig. 53) to the sol of SnO_2, we find that the micell charged by the SnO_3^{--} ion moves to the left, and the K^+ ions migrate to the right. In order to restore electro-neutrality, the dissolved KOH acts in such a way that $2K^+$ ions on the left balance the SnO_3^{--} ion, while $2OH^-$ ions neutralize the K^+ ions displaced to the right. Hence, there has been transported to the cathode an amount of KOH which is the electro-equivalent of the micells migrating to the anode.

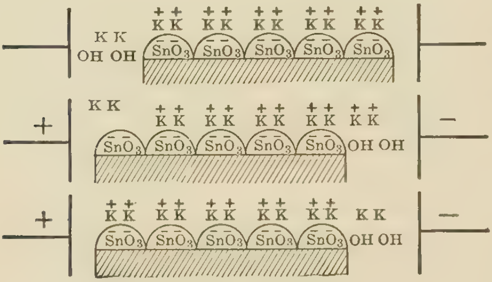

Fig. 53.

Varga, Wintgen, and their co-workers performed their experiments with apparatus similar to those used for determining transport numbers according to Hittorf. If C coulombs pass through the sol, this amount of electricity is transported partly by the ions of the dispersion medium (spec. cond. κ_i), partly by the micells (spec. cond. $\kappa_m = \kappa_s - \kappa_i$ as discussed in eq. (1)). For transporting the latter, $C\frac{\kappa_m}{\kappa_s}$ coulombs are used. If then it is found that β gram-molecules of SnO_2 have been transported, the equivalent aggregation A is found from the equation:

$$A = \beta \frac{96{,}500}{C\frac{\kappa_m}{\kappa_s}}.$$

The figures thus obtained are given in the third column of Table XIX. The agreement with the figures of Column 2 is indeed exceedingly good, considering the difficulties connected with these determinations of transference numbers.

The factor B, discussed above, gives us the total amount of adsorbed alkali. For each equivalent charge, one K ion goes into the outer coating of the double layer; hence, the difference is the amount of K which is present in the micell without participating in the formation of the double layer. This number is shown in the last column of Table XIX, which gives the structure of the micells. Only the factors *n* are still unknown. If we knew the size of the SnO_2 particles, *n* could be computed. Although methods exist for determining particle sizes (Sec. 48) they cannot be used with SnO_2 sols.

Nevertheless, these investigations have greatly advanced our knowledge of the structure of micells and our insight into the composition of the double layer.

It is very interesting to note that not all K_2SnO_3 molecules take part in the formation of the double layer. The researches of VARGA and WINTGEN show that, for the sol with N = 50, about 15 per cent occur in the mobile part of the double layer and 85 per cent are outside. Such a state of affairs may safely be assumed to be a phenomenon of general occurrence (WINTGEN found it to be the case also for Fe_2O_3 and Cr_2O_3 sols); and this in turn confirms our considerations in Sec. 32: Only a part of the double layer is cataphoretically active; the rest must be assumed to belong to the particle, or rather, to the micell.

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CHAPTER VII *

KINETICS OF FLOCCULATION

39. Von Smoluchowski's Theory of Flocculation.—On page 69 it was explained that the mechanism of the flocculation process is governed by two quantities, viz., the probability of collision and the probability of adhesion. It has, furthermore, been shown that for suspensoids the electric charge acts as an obstacle to adhesion. Hence, the foregoing pages have dealt with the manner in which the electric charge as a determining factor for the adhesion can be modified.

Meanwhile, it is important to give an account of the flocculation process in case the probability of adhesion is equal to unity. VON SMOLUCHOWSKI[1] has put forward an interesting theory which has since been confirmed by various experimental investigations. VON SMOLUCHOWSKI's argument may be indicated as follows: When two particles approach each other, the possibility exists that they will unite as soon as the distance between them is sufficiently short. This union is brought about either by the general attraction of matter or by the surface tension (these two quantities being, of course, not at all independent of each other). VON SMOLUCHOWSKI represents each particle as being surrounded by a sphere of attraction, and postulates that when the gravitation point of a second particle enters this sphere, the two particles will unite. Therefore, when the probability of adhesion is equal to unity, i.e., in the absence of repelling forces, the problem of flocculation resolves itself into a discussion of the following questions: (1) How great, for a given sol, is the probability that a particle will enter the sphere of attraction of another particle? and (2), How many doublets, triplets, quadruplets, etc., will be formed after a given interval of time? The answer to the second question will depend upon that given to the first.

Let R be the radius of the sphere of attraction, and r the radius of the particle; then the probability, W, that a moving particle will enter the sphere of attraction of another particle is equal to $4\pi DR$, where D is the coefficient of diffusion which characterizes the velocity (*cf.* Sec. 51). The quantity D has the following value:

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* A more detailed account of the contents of Ch. VII is given by the author in J. ALEXANDER'S Colloid Chemistry, Vol. I, pp. 306–322.

$$D = \frac{k\Theta}{6\pi\eta r},$$

where k is the gas constant divided by N (the Avogadro constant), Θ the absolute temperature,* and η the viscosity of the sol.

Let n_0 be the number of single particles at the start and n_1 the same, after a time t:

$$n_1 = n_0 \cdot e^{-4\pi DRn_0t}$$

Hence the change in the number of particles is given by:

$$-\frac{dn_1}{n_1} = 4\pi DRn_0dt$$

If we consider a change in n_1 which is not too great, integration of this equation gives:

$$n_1 = \frac{n_0}{1 + 4\pi DRn_0t} = \frac{n_0}{1 + \frac{t}{T}}$$

where T is a factor which has been called the time of coagulation. It is equal to $\frac{1}{4\pi DRn_0}$ or, abbreviated, $\frac{1}{\alpha \cdot n_0}$, and has a definite meaning which will be better understood shortly.

So far, we have assumed that the particle into whose sphere of attraction a second particle enters is stationary; but, as a matter of fact, the first particle is likewise in Brownian movement, and hence our equation must account for this:

$$n_1 = \frac{n_0}{1 + \frac{2t}{T}}$$

When we try to extend this reasoning to multiple particles, we are in a quandary as to how the constant, D, depends on the number of particles. If two single spherical particles might be assumed to fuse together, forming one new sphere, with correspondingly increased radius, it would simplify matters; but this assumption conflicts with reality, since as a rule the particles are held together in a cluster.[2] Von Smoluchowski has overcome this difficulty by making the following assumptions: When a particle consisting of i single particles unites with another particle consisting of k single particles, the values D and R for the new particle, consisting of $i + k$ particles, will be:

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* Θ is used here to avoid confusion as T has a different meaning.

$$D_{ik} = D_i + D_k; \quad \text{and} \quad R_{ik} = \tfrac{1}{2}(R_i + R_k).$$

These two assumptions, although extremely simple, are not free from objection.

On the basis of these equations, von Smoluchowski arrives at the following conclusions for the complex particles after a time t, where n_1, n_2, n_3, . . . n_k are, respectively, the number of single, double, triple, and k-fold particles:

$$n_1 = \frac{n_0}{\left(1 + \frac{t}{T}\right)^2} \quad \text{or} \quad \frac{n_0}{(1 + \alpha n_0 t)^2}$$

$$n_2 = n_0 \frac{\alpha n_0 t}{(1 + \alpha n_0 t)^3}$$

. . . .

$$n_k = n_0 \frac{(\alpha n_0 t)^{k-1}}{(1 + \alpha n_0 t)^{k+1}}$$

Von Smoluchowski has further computed the change of the total number of particles, viz., the sum of the single, double, triple, etc., particles, with the time. This number, Σn, after a time t is:

$$\Sigma n = \frac{n_0}{1 + \frac{t}{T}}$$

We now see that the quantity T is the time after which the number of particles, which at the start was n_0, has been reduced to half its original value (for $t = T$, $\Sigma n = \frac{1}{2}n_0$). The coagulation time T is, therefore, the time required to reduce the number of particles originally present to half, and forms an excellent measure of the speed of coagulation.

Figure 54 is a graphic representation of the change in the total number of particles, the number of single particles, the number of double particles, etc., with the time. In this figure the coagulation time, T, is plotted as unity on the axis of abscissae. The general run of these curves will be readily understood. At the start there are only single particles, the number of which (n_1) decreases continually. At first there are no double molecules; later, these appear and increase in number; but after a while they become fewer and fewer, owing to increased formation of triplets, quadruplets, etc. The curve for n_2 shows, therefore, a maximum. The same reasoning holds for triplets, the maximum occurring, however, at a later time, and the number of triplets at the maximum being smaller than the maximum number of doublets. During the coagulation, the total number, Σn, decreases steadily.

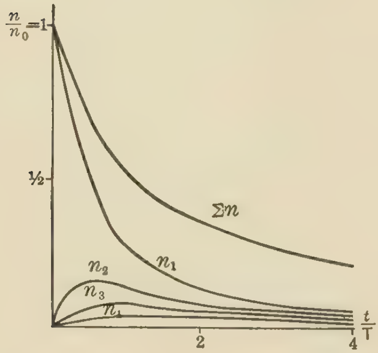

FIG. 54.

The foregoing discussion applies only to cases in which the probability of adhesion is unity, the electric charge of the particles being so small that each collision must necessarily lead to a union of the colliding particles. When the charges are greater, however, not all of the collisions will result in adhesions. We might also say that the sphere of attraction becomes smaller in such cases. Hence, the radius, R, decreases when the probability of adhesion becomes less, and the time, T, simultaneously increases. VON SMOLUCHOWSKI thinks that when the probability of adhesion is less than unity, the numerical course of the flocculation remains the same but the value of T for each probability of adhesion should be multiplied by some factor, ϵ. The curves for different values of the probability of adhesion would be so-called "*affine*" curves. When the probability of adhesion is unity, we speak of rapid coagulation; for values below unity, we speak of slow coagulation. The very definite meanings of these expressions should always be kept in mind. In calculating the value of T from observations of the number of particles, we shall find a definite value for a given probability of adhesion, while for increasing values of the probability of adhesion the values of T will decrease.

40. Experiments on Rapid Coagulation.—In checking the foregoing theory of von Smoluchowski, one has to determine the number of particles of a coagulating sol as a function of the time. In earlier investigations, the change in the number of particles was not measured directly but was derived from some physical properties of the sol, such as the change in viscosity or the change in light absorption,[3] which were thought to be a direct measure of the coagulation process. It has been shown, however, that all these investigations are much more difficult to interpret than those in which the number of particles is measured directly. Experiments of the latter kind have been performed by Zsigmondy [4] and his pupils on the gold sol, and by Kruyt and van Arkel [5] on the sol of selenium.

According to the above theory, we can determine either the change in the number of single particles (this is feasible in the case of the gold sol since these differ from the multiple particles in color, when viewed in the ultramicroscope) or the change in the total number. The second method is the easier and is therefore more often applied. The coagulation is allowed to proceed for a certain length of time; it is then interrupted and the particles counted in the manner described later (see p. 140). The coagulation can be successfully arrested in many cases by the addition of a protective colloid, such as gelatin. The following table gives the measurements of Westgren and Reitstötter

TABLE XX

Gold Sol. Particles of 96 mμ Diameter. Coagulated by NaCl, 86 Millimoles per Liter. Sol Concentration 5.22×10^8 Particles per cc.

t Time in minutes	10^{-8} number of particles per cc.	T coagulation time in minutes	Calculated number of particles $\times 10^{-8}$ for $T = 5.3$ min.
0	5.22	....	5.22
1	4.35	5.0	4.39
2	3.63	4.6	3.78
3	3.38	5.5	3.33
5	2.75	5.6	2.68
7	2.31	5.5	2.25

for the gold sol. It will be seen that the value of T is constant and that the agreement between the number of particles after different periods of time, as found and as calculated, is satisfactory. The same agreement was obtained for the sol of selenium by KRUYT and VAN ARKEL. From the equations given on page 118 we can deduce easily that the time of coagulation must be proportional to the viscosity and inversely proportional to the absolute temperature. This was confirmed by LACHS and GOLDBERG with a gold sol.[5]*

41. Müller's Theory of Flocculation.—The theory of VON SMOLUCHOWSKI was derived for an isodisperse sol, viz., for a sol containing particles of equal size. HANS MÜLLER [6] has given an outline of what is to be expected when the particles are not all of the same size. The simplest case is that in which there are only two kinds of particles: large ones with radius r_l and small ones with radius r_s. Assuming, as before, that there must be material contact to bring about coalescence, MÜLLER takes R, the radius of the sphere of attraction, equal to $(r_l + r_s)$. The probability W that a small particle enters the sphere of attraction of a large particle is given by the equation:

$$W = 2\pi(r_l + r_s)\cdot(D_l + D_s)$$

(on page 118 the value for W was represented by $4\pi RD = 2\pi R \times 2D$). Substituting the values for D_l and D_s (for which see p. 118) we find:

$$W = 2\pi(r_l + r_s)\cdot\left(\frac{k\Theta}{6\pi\eta r_l} + \frac{k\Theta}{6\pi\eta r_s}\right) = \frac{k\Theta}{3\eta}\cdot\frac{(r_l + r_s)^2}{r_l r_s}.$$

The probability w that a small particle comes within the sphere of another small particle (with same radius r_s) is represented by:

$$w = \frac{k\Theta}{3\eta}\cdot\frac{4r_s^2}{r_s^2} = \frac{4k\Theta}{3\eta}.$$

The ratio of these two probabilities is:

$$\frac{W}{w} = \frac{(r_l + r_s)^2}{4r_l r_s} = \frac{\left(1 + \frac{r_l}{r_s}\right)^2}{4\frac{r_l}{r_s}} = \frac{(1 + f)^2}{4f},$$

where $f = \dfrac{r_l}{r_s}$.

Considering that f is greater than unity, we find that the probability that a small particle added on to a large one is greater than the probability that it unites with another small particle and this probability becomes greater the more pronounced the difference in size.

By taking into account the respective *numbers* of large and small particles we can further develop MÜLLER's equation for the kinetics of flocculation, for which the reader is referred to the original paper. The preceding discussion is sufficient to understand certain facts mentioned in the literature. Years ago, WIEGNER [7] and also VON GALECKI [8] noticed that the small particles of a heterodisperse sol disappear rapidly due to the fact that the large particles act as nuclei for coagulation. Extensive researches of WIEGNER and TUORILA [6] have confirmed the applicability of MÜLLER's extension of the theory of VON SMOLUCHOWSKI. TUORILA,[9] moreover, has made a detailed study of the settling of large particles (so-called orthokinetic flocculation) and its effect on the removal of small ones, a problem of considerable importance for agriculture.

42. Experiments on Slow Coagulation.—From the standpoint of colloid chemistry, the study of slow coagulation is far more interesting than that of rapid coagulation. The latter is merely the investigation of a sol that has been robbed of its electric charge and hence can hardly be called a sol; in fact, the study of rapid coagulation is the anatomy of the dead body of a colloidal solution! The results, therefore, confirm the trend of ideas underlying statistical kinetics but can teach us nothing regarding the stability of a colloidal solution. Slow coagulation, on the other hand, is a kind of patholological physiology of the sol, and, when the probability of adhesion is changed systematically, it may deepen our insight into the stability of sols.

Unfortunately, very little work has been done in this field. The researches of WESTGREN seem to give a more or less satisfactory agreement with the theory of VON SMOLUCHOWSKI. The experiments of KRUYT and VAN ARKEL, however, have decidedly demonstrated that the simple assumption of VON SMOLUCHOWSKI, as regards the multiplication of the coagulation time, T by a constant factor, ϵ, is incorrect. In Table XXI is given the computation of the coagulation time, T, for the selenium sol when slow flocculation occurs. It is seen that T is not at all constant,

TABLE XXI

SELENIUM SOL. PARTICLES OF 52 mμ. COAGULATED BY KCl, 59 MILLIMOLES PER LITER. SOL OF 29.7×10^8 PARTICLES PER CC.

t Time in hours	10^{-8} number of particles per cc.	T Time in hours
0	29.70	
0.66	20.90	1.5
4.25	19.10	7.6
19	14.40	18
43	10.70	24
73	7.70	25
167	6.45	46

and hence the curve for slow flocculation is not "*affine*" with that for rapid coagulation. The fact that T increases means that the coagulation gradually slows down; in other words, the probability of cohesion decreases the larger the aggregates that are formed. This, in turn, might be explained as follows:[10] Presumably there is no uniform discharge over the whole surface of the particle so that in some places the potential is above the critical value and elsewhere below ζ_{cr}. Cohesion occurs in those spots where the discharge has proceeded farthest and as a result of this, the parts with higher charge are turned outside. The larger the size of the aggregates the smaller the possibility for other particles to unite with them.

43. Some Applications of the Preceding Trend of Thought.—The question obviously arises: What is the significance of the flocculation value in the light of the preceding theories of coagulation? As stated on page 69, the flocculation value is the quantity of electrolyte which completely precipitates the sol in a given time and in such a manner that a complete settling of the flakes shows the end of the flocculation process. The impression prevails that this condition is reached only when we are in the region of rapid coagulation. In the case of the gold sol, the blue coloration is always used as a criterion for flocculation, since this change of color, occurring within a few minutes, is indeed an indication that the sol will settle within a few hours. The region of rapid coagulation lies at about the same concentration as that at which the color change is observed. The selenium sol likewise shows a change in color: when flocculation occurs a peculiar greenish hue appears. This tint is noticed both at the flocculation value and at concentrations producing rapid coagulation.

The flocculation value, which played such an important part in previous discussions, is therefore, to a certain extent, the concentration at which the probability of adhesion closely approaches unit value. It is evident that the statements made on page 78, regarding the relation between concentration of the sol and flocculation value, are based on the idea that the value 1 for the probability of adhesion is never actually attained. Since we mean by critical potential (*cf.* p. 68) the potential of the particles at the flocculation value, we overlook the fact that this definition depends on the probability of adhesion which exists when the particle is discharged at the flocculation value. If we try to picture to ourselves the connection between probability of adhesion and potential, we arrive at the following presentation:

Figure 55 is an extension of Fig. 44 on page 89. A third graph has been added here,[11] however, viz., the change in the probability of adhesion, K, due to different values of the potential, ζ. The curve drawn in Fig. 55 is a schematic representation of the probable relation for sulphide sol. The value of K varies from 0 to 1; it is 0 for high values of the potential and is 1 when the potential is 0. Experience teaches that at small concentrations of electrolyte, i.e., in the region of large values for ζ, there is no appreciable change in the sol. Starting from a certain concentration, flocculation is more or less noticeable; hence, the curve representing K as a function of ζ starts to rise at a certain value and continues to rise thereafter. Looking at the curve from the value $K = 1$, we have to consider the fact that the velocity of flocculation changes little or not at all at values of potential lying between O and the critical potential. Hence in this part of the curve, too, there is little change of K when ζ varies. The whole curve, consequently, assumes an S-shaped course with a point of inflexion.

For a gold sol, however, it appears that the probability of adhesion changes in a different manner when the boundary charge is changed. Investigations of Zsigmondy and his pupils[8] have shown that, beginning at a certain concentration below which there is hardly any flocculation, a slight increase in electrolyte concentration causes a sudden and decided increase in the velocity of flocculation, and that, for still higher concentrations, the velocity becomes rather independent of the concentration. The relation between K and ζ in the case of the gold sol is shown separately in Fig. 55 *bis*, to bring out clearly the difference in the properties of these sols.

Kruyt, in the article just quoted, has demonstrated that this difference in the relation between probability of adhesion and charge enables us to explain why sulphide sols show a relation between flocculation value and concentration of sol different from that of the gold sols discussed on page 79.

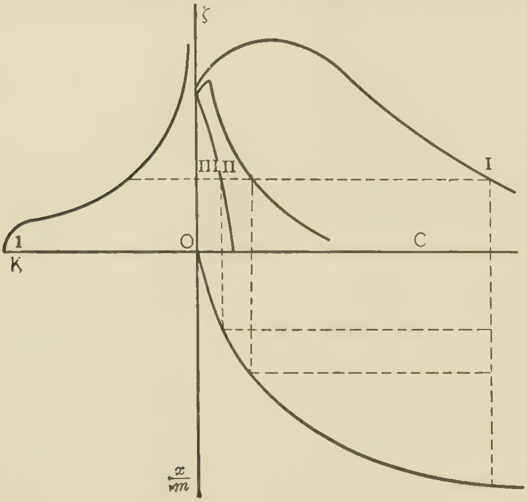

Fig. 55.

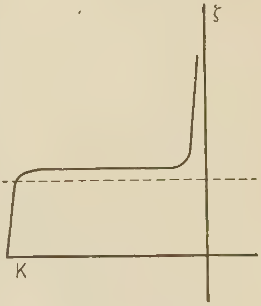

Fig. 55 *bis*.

Flocculation value and critical potential are, therefore, ideas which, while not directly applicable to definite types of dispersoids, have, nevertheless, a striking significance for those concentrations at which rapid changes in the probability of adhesion occur. Although the theory of von Smoluchowski infers that the velocity of coagulation is a variable quantity, the flocculation value is a characteristic entity in all possible flocculation phenomena. Consequently, it has been possible, in preceding chapters, to draw valuable conclusions concerning flocculation values.

Another question that might come up for discussion is the following: Why should we speak at all of *probability* of adhesion?

It is conceivable that no union may take place above a certain potential and that a lasting union may occur below that potential. Freundlich [12] has made valuable contributions to our understanding of this problem.

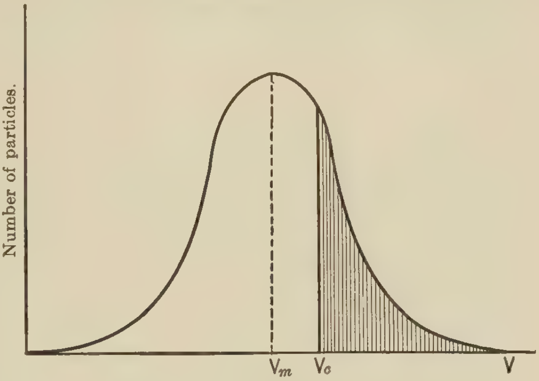

Fig. 56.

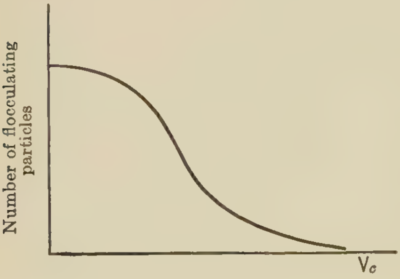

Fig. 57.

A particle that is somewhat charged is unable, at a certain temperature, to penetrate the repelling sphere of a second particle. If it had a greater speed it might possibly enter into that sphere, provided it were shot into the double layer at right angles by the Brownian movement. We know, however, that all particles have not the same velocity. The temperature determines only the *average* speed of the particles. The distribution of the velocities is in agreement with the well-known theory of Maxwell. In Fig. 56 the number of particles, for a given temperature, are plotted as ordinates against the velocities as abscissae. V_m is the average velocity, which naturally occurs most frequently for that temperature. If we assume that a certain critical velocity, V_c, is required to enable a particle to penetrate the repelling sphere under the stated conditions, this assumption would, *a fortiori*, also apply to particles with velocities higher than V_c. The ratio between effective and non-effective collisions is given by that between the cross-hatched area and the unshaded portion of Fig. 56. The probability of adhesion is, then the ratio between the cross-hatched portion and the total area below the curve. Freundlich, furthermore, calculated how the number of particles in condition for flocculation depends on the location of V_c in the figure: the higher the charge of the particles, the more the position of V_c shifts to the right (in Fig. 56). FREUNDLICH's result is reproduced in Fig. 57. It is readily understood that this figure resembles the $\zeta - K$ portion of Figs. 55 and 55 *bis*, since the number of particles fit for coagulation corresponds to the probability of adhesion, K, while the critical velocity, Vc, corresponds to the charge, ζ, of the particles.

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CHAPTER VIII

OPTICAL PROPERTIES OF SUSPENSOIDS

Following a brief introduction (Chapter I) our attention has hitherto been principally focussed on the dynamic phenomena of suspensoids, which have enabled us to understand how colloidal systems are built up and particularly how their stability is attained and lost. On the basis of this knowledge, we shall now examine the static properties of suspensoids, and of these, first of all, the optical properties.

44. Tyndall Phenomenon.—The TYNDALL effect has already been mentioned, on page 6. It is, generally speaking, caused by particles, smaller than the wave length of the light, which scatter the light, thereby polarizing it at the same time. While fluorescent light is polarized slightly or not at all,[1] colloidal solutions show characteristic polarization.

It is, however, not an easy task to make solutions that do not exhibit the TYNDALL phenomenon in any degree. So-called optically void water requires a very special preparation. Distilled water, however carefully prepared, is never completely optically empty. SPRING [2] has shown that optically empty liquids may be obtained by allowing a voluminous precipitate to pass through a solution. Into a solution of $ZnSO_4$ he introduced so much alkali that the zinc hydroxide settled as a voluminous precipitate. The supernatant liquid was then practically optically void.

SPRING obtained the same result with other salt solutions, but not with those which on hydrolysis produce colloidal constituents. Alum solutions, for instance, invariably showed the TYNDALL effect due to the presence of colloidal Al_2O_3.

It was for a long time believed, as a result of experiments performed by LOBRY DE BRUYN,[3] that sugar solutions also showed a permanent TYNDALL effect. Recent investigations by WOLSKI,[4] however, have shown that the phenomenon can be eliminated in sugar solutions.

Rayleigh [5] has derived the following relation between the intensity, I, of the light scattered sidewise, the volume, v, of the obstructing particle, the distance, d, between observer and particle, and the wave length, λ, of the scattered light:

$$I = f\left(\frac{v^2}{d^2\lambda^4}\right).$$

The formula, however, holds only for insulators; it is not applicable to particles made of materials that are good conductors of electricity.

This formula makes it clear why substances like sulphur, mastic, gamboge, etc., show a peculiar bluish Tyndall light. From the above equation, with λ^4 in the denominator, it follows that when non-conductors are dispersed, *small* wave lengths are favored, and hence the blue color predominates in the Tyndall light.

Rayleigh also explained the blue color of the sky from the same point of view. The blue sky light is simply the Tyndall light originating from the passing of the sunlight through the atmosphere. The molecules of the air and, more especially accidental differences in density are sufficient to explain the Tyndall light, and the blue color agrees with the foregoing formula of Rayleigh.

The blue color of such fluids as diluted milk is also readily understood from the above explanation. We thus see why it is necessary to distinguish between the color due to light absorption and the color of the Tyndall light. The non-recognition of this distinction leads to misunderstanding and no doubt played a part in Goethe's theory of colors.

It should be noted that Rayleigh's equation obtains only, as stated above, for extremely small particles of a non-conducting substance. In the case of gold particles, for instance, the conditions are somewhat different. For these, Mie [6] has proposed a theory which has led to the result that is represented graphically in Figs. 58 and 59. The dot in the center of each of these figures indicates the gold particle. The arrows show the direction from which the light strikes the particle. The total intensity of the diffracted light in any direction is given by the portion of the radius vector inside the outer curve, while the portion cut off by the inner curve indicates the fraction that is not polarized. Hence, the portion between the two curves gives the part of the diffracted light that is polarized. From Fig. 58, drawn for a so-called "infinitely" small particle, it is seen that the light which is scattered in a direction at right angles to the path of the incident ray is completely polarized, and that in all other directions the light is only partially polarized. Fig. 59 gives the radiation diagram for a much larger particle. In this case the light is never completely polarized; moreover, the maximum polarization is not located in a direction perpendicular to the path of the ray but at an angle of about 120. Mie's theory thus connects the size of the particle with the polarization of the Tyndall light. The latter is completely polarized only in the limiting case of an infinitely small particle for an angle of diffraction of 90°.

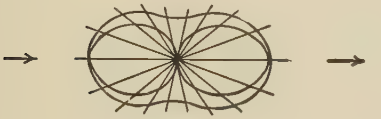


Fig. 58.

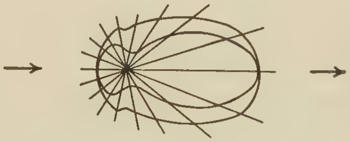


Fig. 59.

45. Color of Suspensoids.—In the previous section we considered the nature of the diffracted (Tyndall) light. We shall now discuss the light that is transmitted, or adsorbed, viz., the *color* of the solutions.

Color is, indeed, a characteristic property of colloidal solutions. A dilute solution of ferric chloride is slightly yellow; when this solution is poured into boiling water, a colloidal solution of Fe_2O_3 is formed by hydrolysis, and thus, with the same amount of iron, a deep red liquid is produced. Sols show strong coloration, and have more pronounced absorption bands than the corresponding molecularly or ionically dispersed systems.

It is obvious that some relation exists between the size of the dispersed particle and the light absorption. The phenomenon of the change in color from red to blue, exhibited by a gold sol at the beginning of coagulation, has been known for years and has led to the search for a direct connection between light absorption and size of particle. This relation, however, can evidently be simple only when the shape of the particles is comparable, i.e., when we are dealing, for instance, with spherical particles of different radius. When a sol flocculates, however, the particles coagulate in the form of warty lumps (*cf.* p. 119) so that not merely the radius but also the shape of the surface and the density of the particle taken as a whole are changed. This is no doubt an important factor in the case of the gold sol, because we are not at all sure that a highly dispersed gold sol is red and a slightly dispersed sol blue. On the contrary, it is quite possible to prepare a blue gold sol which is more dispersed than one that looks red.

Zsigmondy[8] found that, in general, a sol consisting exclusively of primary particles appears red, while the agglomeration of such spherical particles to multiple particles causes a change to blue. All blue gold sols, therefore, have undergone coagulation to some extent.

A number of investigators have studied the relation between light absorption and the size of the particles when the latter are present solely as primary particles of varying radius. It has been found that both the wave length which is most absorbed and the maximum absorption depend on the size of the particle. In Fig. 60 is plotted the light absorption as ordinate against the wave length as abscissa, for five different gold sols with varying degrees of dispersion, No. 1 being the coarsest sol and No. 5 the most highly dispersed. It will be seen that an increase in the degree of dispersion displaces the maximum in the direction of the smaller wave lengths, and that, at the same time, the maximum value first rises and then decreases.[9] The intensity of the color, therefore, first increases and afterwards decreases, with simultaneous displacement toward smaller wave lengths.

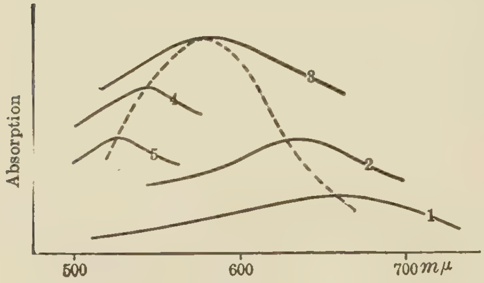
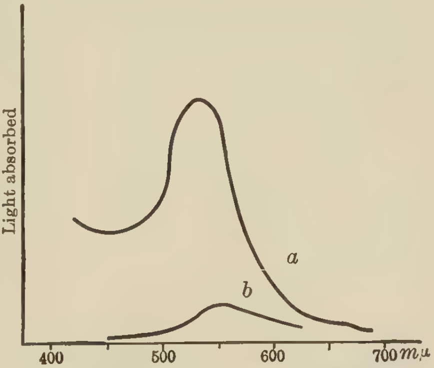


Fig. 60.

Svedberg has made use of this phenomenon to demonstrate that colloidal solutions, as their degree of dispersion increases, approach the condition of molecularly dispersed systems. He considers this an argument for the real existence of molecules, i.e., for the discontinuity of matter. The results which he has obtained with the sols of sulphur and selenium are favorable to this idea.

It might be assumed that the color of colloidal solutions is greatly influenced by the fact that light of a certain wave length is scattered as Tyndall light, thus showing a certain analogy to fluorescence. Experiments by Steubing,[10] however, have shown that the intensity of the Tyndall light is only a small fraction of the total absorbed light. In Fig. 61, both intensities are reproduced for the same sol, the wave length being plotted as abscissa. The figure shows that the diffracted light is only a small portion of the absorbed light and that the maxima do not coincide.



(a) Total light absorbed; (b) Tyndall light.

Fig. 61.

46. Behavior toward X-rays.—The investigations of von Laue and of Sir Wm. Bragg and W. L. Bragg [11] have indicated that the face of a crystal acts as a grating toward a pencil of X-rays

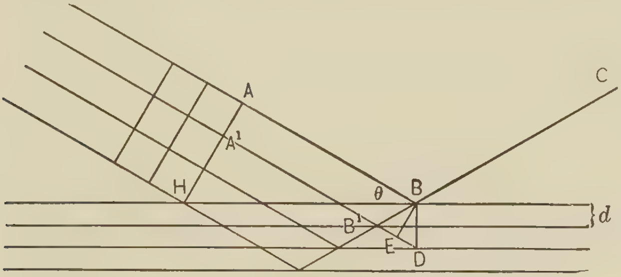


Fig. 62.

The molecules (later investigations have shown that atoms are involved) are arranged in definite planes, placed at distances which are of the same order of magnitude as the wave length of

X-rays. In Fig. 62 the horizontal lines represent a number of these planes. A pencil of X-rays, AH, strikes the crystal and is reflected by the planes drawn in the figure. Let BC be the path of reflection. The difference between the paths ABC and $A'B'C$ is given by:

$$B'B - B'E = B'D - B'E = ED.$$

Furthermore:

$$ED = 2d \sin \theta,$$

where d is the distance between the planes and θ the glancing angle.

There will be interference when the following equations hold:

$$\lambda = 2d \sin \theta \text{ (first order)}$$

$$2\lambda = 2d \sin \theta \text{ (second order)}$$

. . . .

$$n\lambda = 2d \sin \theta \text{ (}n\text{th order).}$$

Hence, a ray of light falling on a thin lamella of a given crystal gives rise to interference figures which are characteristic of that particular crystal.

Debye and Scherrer[12] have modified this method for the recognition of crystals in such a way that it is no longer necessary to use a crystal *plate*. When a beam of X-rays hits a quantity of finely divided (powdered) crystals in which the separate fragments lie in all orientations, an interference pattern characteristic of the faces of the crystal fragments is, nevertheless, produced, and what we obtain is a circular interference pattern, as shown in Fig. 63.

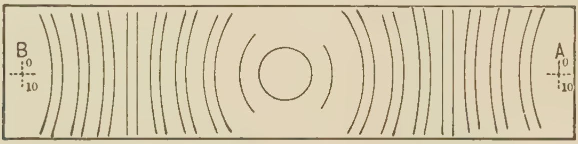


Fig. 63.

Thanks to this method it is possible to study both powders and colloidal systems to find out whether they consist of crystalline constituents, and, if so, what the nature of the crystals really is. Debye and Scherrer have shown how these photograms can be used to compute the crystal system and the size of the particle.

The application of this method to colloidal systems and to the precipitates resulting from the coagulation of the colloids has led to the conclusion that the particles in nearly all suspensoid sols are crystalline. For instance, with respect to the gold sol, Debye and Scherrer found that the particles consist of tiny crystals having the same elementary cube as gold powder and belonging to the same crystal system. The size of the particles agreed completely with determinations made along different lines, which will be discussed fully in the following section. The highest dispersed gold sol studied by the above authors appeared to consist of particles having a parameter of 1.8 $m\mu$, while a computation of the number of atoms in such a particle showed that there were not more than 5 atoms to the side of the cube.

Characteristic crystal spectra were also found for a silver and for an As_2S_3 sol.

It has thus been proved that in many cases colloidal particles are crystalline and that, consequently, it is superfluous to discriminate between crystalline and colloidal substances (*cf. p.* 8).

47. Ultramicroscopy.—On page 5 it was stated that we are unable to note the presence of particles suspended in the liquid when looking at a suspensoid sol through an ordinary microscope. The particles are usually much smaller than the wave length of the light, and hence it is impossible to visualize them. One of these particles, when viewed in transmitted light, no doubt disturbs the beam of light to some extent, but this disturbance is so small as to escape notice, just as the feeble light of a star cannot be observed in the day-time. In order to make sure of the presence of a colloidal particle, it becomes necessary to devise an apparatus which will separate the interference phenomenon caused by such a particle, from the incident light.

Such an instrument was first constructed by Siedentopf and Zsigmondy [13] and is called an ultramicroscope. It depends, generally speaking, on the principle that the light used for illuminating the object does not reach the observer directly but only eventually in the form of an interference phenomenon. In other words, the particle is noticeable only by a light effect on a dark background (dark-field illumination).

This principle, which forms the basis of the microscope devised by Siedentopf and Zsigmondy, is illustrated in a simple manner in Fig. 64. The illuminating beam of light follows a horizontal path, while the microscope is placed vertically; when there is no object in the field, nothing but darkness will be observed through the microscope. If, however, a particle is present in the field of the microscope and in the path of the light ray, a diffraction phenomenon becomes visible in the form of a colored ring. Such a diffraction ring is an indication of the presence of a small particle but should not be considered as an *image* of the particle.

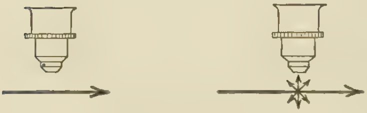


Fig. 64.

In other words, the ultramicroscope is a refined method of observing the Tyndall effect, since we observe, so to speak, the Tyndall phenomenon for each particle separately. Figure 65 shows the ultramicroscope in its original form. The light from the arc lamp, *d*, reaches the microscope through the lenses, *f* and *h*, and the movable eyepiece, *l*. The sample is thus lighted from the side and is examined through the microscope, *i*. The colloidal solution is placed in a cuvette, which in modern instruments has the form devised by Biltz (Fig. 66). It has a little window in front to admit the light for the illumination, and another one facing the objective for the observation of the diffracted light. The great advantage of this cuvette lies in its easy manipulation. The solution to be observed is

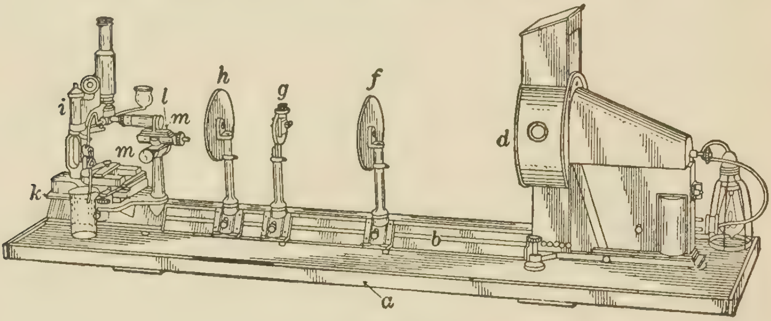


Fig. 65.

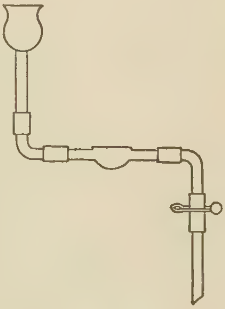


Fig. 66.

poured into the little funnel, and then allowed to flow out, by opening the pinchcock. In general, it is sufficient to rinse the cuvette three times in order to obtain a clear image of the sample.

By means of a cuvette holder, the cuvette is firmly attached to the tube of the microscope. A sharp focus is made possible by another device, which has, moreover, a second advantage. This is the slit, *g*, which is shown separately and enlarged in Fig. 67. Two sets of movable screens enclose a slit, the height and width of which can be varied. By means of the screw, *a*, the width can be changed, while the micrometer screw, *c*, regulates the height of the slit; hence, only an exceedingly thin beam of light enters the sample. By moving the tube up or down, we only move the focus with respect to a stationary illuminated disk, and sharp focussing is thus made possible. The second advantage of this slit device is that we take, so to speak, a thin slice (*coupe*) out of the sample, not mechanically but optically. Before observing a specimen under the ordinary microscope, we slice off *mechanically* a thin section to avoid being disturbed by blurred images of objects higher or lower than the one under examination. The same result is obtained here by illuminating only a very thin layer of the sample.

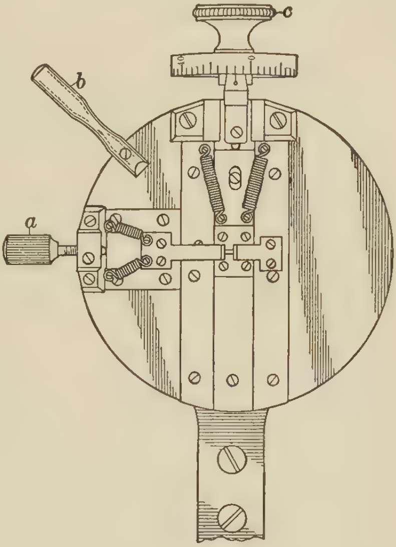


Fig. 67.

In addition to the original ultramicroscopic apparatus, a number of other systems have come into use in the course of time. The slit-ultramicroscopic arrangement might be called a system with *orthogonal* illumination, since observation and illumination take place at right angles to each other. Several other systems use *co-axial* illumination, whereby the direction of the incident ray coincides with the direction in which we observe the specimen.

This, however, would, as we have seen, preclude direct ultramicroscopic observation, and hence some sort of artifice is required to prevent the illuminating ray from reaching the observer.

The simplest way to do this consists in the application of a central diaphragm inside the condenser of the illuminating system (Fig. 68). The middle part of the light cone is cut off, and the remaining part, which leaves the condenser at an obtuse angle, lights the sample through the immersed drop. After passing through the sample, the light is totally reflected against the cover glass, and no direct light reaches the observer. Only light disturbances caused by particles that may be present are noticed, so that here again we have conditions favorable for ultramicroscopic observation. A great disadvantage of this system is the fact that only the outer rays are used and the best part of the light cone is cut off. The modern condensers used for ultramicroscopic work obviate this difficulty.

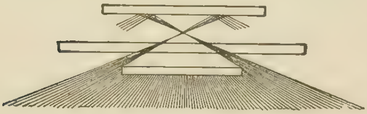


Fig. 68.

Figure 69 shows the *paraboloid* condenser. The side faces of this condenser consist of a parabolic mirror surface. The tip of the light cone is again located in the specimen and direct observation of the light beam can be prevented by using an objective having an aperture smaller than that of the light cone. Under those conditions it is, therefore, impossible to observe the light directly, and only diffraction images appear on a dark background.

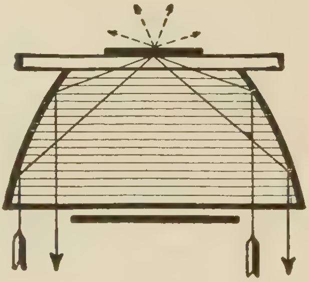


Fig. 69.

The principle of this condenser is repeated in several other types, represented in Figs. 70 and 71 and known as cardioid and mirror condensers, respectively. The excellence of all these devices depends on their providing for maximum illumination of the sample, which they cannot do unless the tip of the light cone is a perfect point. The cardioid condenser no doubt approaches this ideal most closely. This condenser cannot be used to advantage, however, unless the glass slide, the cover glass, and the depth of the specimen meet rigid specifications. For this reason, these instruments, although otherwise excellent, are, as a rule, not well adapted for use in colloid-chemical laboratories, where the classical slit-ultramicroscope still remains the most practical instrument at least, insofar as liquid systems are concerned.

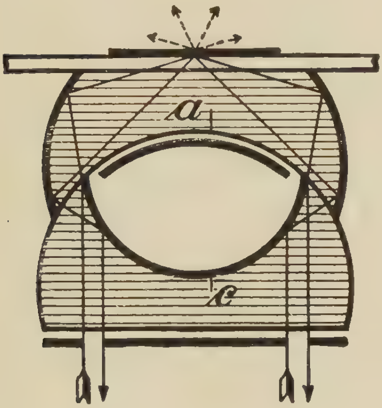


Fig. 70.

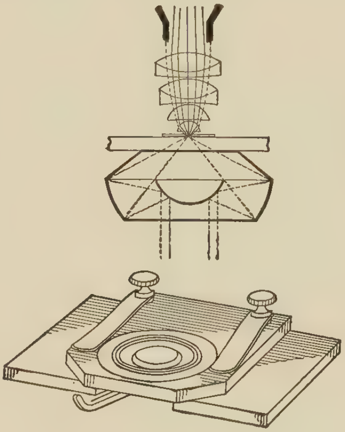


Fig. 71.

The slit-ultramicroscope has recently been modified in such a way that the cuvette is omitted entirely (Fig. 72). The objective of the horizontal illuminating system is so close to the objective of the microscope that a drop of the sol can simply be suspended between the two objectives. The sol thus acts as immersion liquid and as specimen at the same time. The new instrument, called the immersion ultramicroscope, enables one to obtain a greater resolving power (particles of 4 mμ are visible); but, on the other hand, the freely suspended drop is the cause of rapidly changing microscopic images.

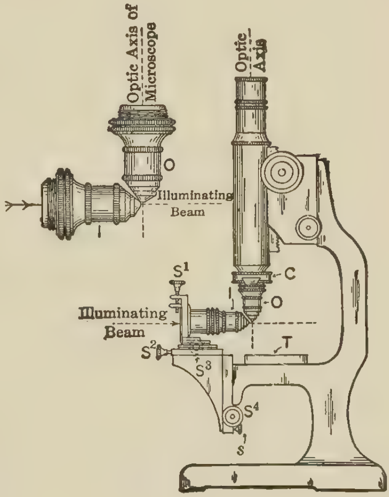


Fig. 72.

The ultramicroscope of COTTON and MOUTON[14] should also be mentioned. A block of glass, as sketched in Fig. 73, is used as condenser. The light of the incident beam strikes the sample at an angle and is totally reflected against the cover glass. This system, therefore, stands between those using orthogonal and those employing co-axial illumination.

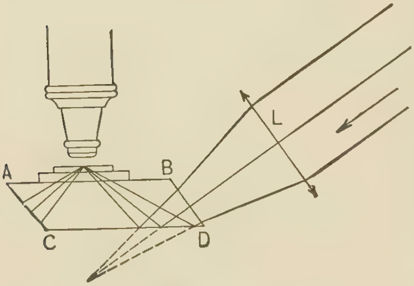


FIG. 73.

48. Determination of the Particle Size.—It was stated previously that in the ultramicroscope we observe only the interference rings caused by the particles and that these, as a rule, are not a measure of the size of the particles. Since the knowledge of the size of the particles is of great importance in colloid chemistry, different ways of evolving a suitable method have been tried out.

The most direct way that has been successfully followed, for instance, for gold sols, is that which makes use of the ultramicroscope. Let us consider a sol containing a known weight of gold per liter. Assuming, for the present, that the particles have the same density as a piece of solid gold, we also know what the total volume of the gold particles is. All that remains to be determined is the number of particles into which this amount of gold is divided. In order to do this we have to count the number of particles in a definitely known volume. Since the count has to be carried out in the ultramicroscope, the field of vision must be defined in a precise manner. To this end, an EHRLICH diaphragm is placed in the eyepiece and a solution of fluorescein poured into the cuvette in order to obtain a bright green field which will enable us to measure the length and breadth of the visible field by means of an eyepiece micrometer. Using the slit-ultramicroscope, we can determine the depth of the illuminated volume of liquid by turning the slit through 90° (Fig. 67). What was depth before now becomes breadth and can be measured with the eyepiece micrometer. In the cardioid microscope, the height of the chamber is determined by first focussing the cover glass and then the glass slide. The distance between them is read on the micrometer screw of the microscope. This distance is so small that all particles present in the enclosed area can be observed by focussing the midway plane. Having thus accurately determined the size of the blocked field, one pours the sol into the cuvette. The dilution is so chosen that there are only two or three particles, on the average, in the field. Since the particles are in Brownian movement, the number does not remain constant; hence, it becomes necessary to take the mean of 100 to 200 counts. From the number of particles in the dilute sol, it is easy to compute the number present in 1 liter of the original sol. If we imagine the particles to be spherical, the volume of a single particle can be calculated.

In this way, the *average* size of the particles is found. The results are, however, only reliable when we are sure that no amicroscopic particles are present in the sol, in other words, that *all* particles in the blocked volume have actually been counted.

Zsigmondy[13] applied an ingenious method of measuring the size of an *amicroscopic* gold sol. He observed that reduction of $AuCl_3$, in the presence of colloidal gold particles, results in the precipitation of the gold on the preëxisting gold particles (for further particulars, see p. 163). These, therefore, grow without increasing in number, until well above the limit of ultramicroscopic visibility. The count of these visible microns corresponds to that present in the amicroscopic sol. This number, together with the known concentration of the original sol, gives the size of the amicroscopic particles.

Since we know how many molecules are present in a gram-molecule, viz., the so-called Avogadro constant: $N = 60.6 \times 10^{22}$, we also know the size of the molecules. While the dimensions of colloidal particles usually lie between 2 and 200 $m\mu$, those of molecules lie as a rule below 1 $m\mu$. In Fig. 74 is given a schematic summary of the size of various particles with dimensions ranging from that of a blood corpuscle to that of a hydrogen molecule. Since these dimensions vary enormously, the figure is drawn to three different scales, as indicated by the accompanying text. In each case the last example of a preceding scale is repeated (enlarged) on the next scale.

For measuring colloidal particles that are not too small, there is another method, which consists in determining the speed with which the particles settle.

For instance, a selenium sol, prepared in the following manner, may be employed:

$$SeO_2 + N_2H_4 = Se + 2H_2O + N_2$$

The method used is that of particle growth, applied to gold sols by Zsigmondy (p. 141), viz.: to the first-formed Se sol more SeO_2 and hydrazine are added. In this way comparatively coarse particles are obtained. If this sol is allowed to stand in a graduated tube, it will be seen that the orange-colored selenium particles settle after a while. The velocity of settling is measured and the size of the particles determined by means of Stokes' law. This law is mathematically expressed by the formula:

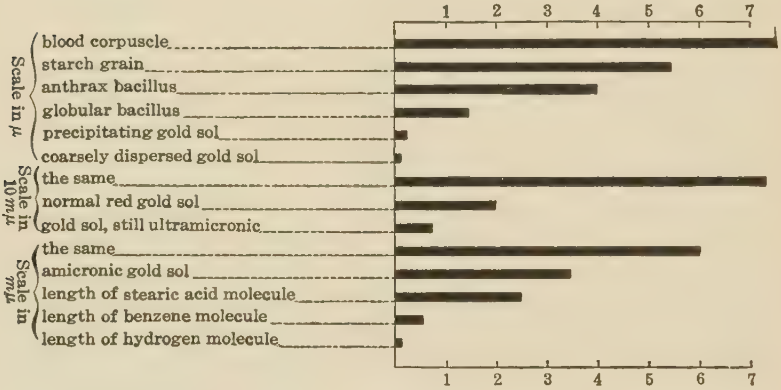


Fig. 74.

$$W = 6\pi\eta r s,$$

where η is the viscosity of the medium, r the radius of the particle, s the steady rate of falling, and W the force of friction, which in this case is equal to $\frac{4}{3}\pi r^3(d_{\text{particle}} - d_{\text{medium}})g$ (*cf.* Sec. 51). In this latter expression d is the density and g the acceleration due to gravity. Using this method, van Arkel[15] found for the radius of the particles in a selenium sol a value of 63 mμ, while the value obtained by counting was 50 mμ.

This drop method is obviously applicable only in the case of coarse suspensions; to this end it has been modified in several different ways.[16]

The centrifugal force works in a manner similar to the force of gravitation; centrifugal sedimentation is, therefore, also a measure of the particle size. In order to apply this method to colloidal systems Svedberg constructed an ultracentrifuge having a force of sedimentation 100,000 times as strong as the force of gravitation.[16a]

The difficulties involved in the use of this method lie in the evaluation of the experimental data, a problem that has never been satisfactorily solved, particularly in the case of polydisperse systems.

A number of other physical properties have been tried for the determination of the size of particles in sols,[17] but these as a rule, are rather unsatisfactory.

Finally, we recalled the statement made in Sec. 46 that the method of X-ray analysis also gives us an idea regarding the size of colloidal particles.

49. Double-refracting Sols.—Under certain conditions, some sols show the remarkable property of double refraction. This was originally discovered for the Fe_2O_3 sol,[18] but the first systematic investigation was made with the aid of the sol of V_2O_5. Freundlich and Diesselhorst [19] had already observed that this sol, prepared by the method of Biltz,[20] appeared to be double-refracting, at least after some time, when allowed to run through a tube. The same phenomenon could be seen between crossed nicols on placing the sol in an electric or magnetic field. The reddish-brown sol exhibits this peculiar property of becoming double-refracting by the dark streaks which appear on shaking and vanish when the liquid is left alone. Ultramicroscopically, it was found that the sol contained elongated particles. Although the interference picture in the ultramicroscope cannot give direct evidence of the shape of the particles, it is nevertheless a fact that a very pronounced one-sided development of the particles produces a correspondingly shaped diffraction image. Hence, we notice, in the case of the V_2O_5 sol, *long needles* instead of rings as in the case of other sols.

A further ultramicroscopic study [21] has confirmed the conjecture of Freundlich and Dieselhorst; hence the above phenomenon is to be explained as follows: When the sol is set in motion, as for instance, by allowing it to flow through a tube, the particles arrange themselves lengthwise in the direction of flow, so that a minimum of friction is encountered. Likewise, when cataphoretic motion is caused by an electric field, or when a magnetic field is produced, an orientation of the particles in the direction of the stream lines is effected.

Being crystalline and double-refracting, the particles, when placed with their optical axes all in one direction, act as one unit, and the sol as such shows double refraction. If the particles lie unoriented, they will cause certain disturbances in the path of transmitted rays, but the particles are too small, and these disturbances too insignificant, to give rise to a perceptible turbidity. However, if one *stirs* the sol a localized phenomenon of orientation is produced and coöperation of parallel particles in stream lines takes place, thereby causing an apparent turbidity.

It is evident that not only needle-shaped particles but also disk-like particles show similar phenomena. The above-mentioned investigators found corresponding phenomena for sols that did not consist of elongated particles; the fact that these particles were disk-shaped was demonstrated in the following manner.

When the particles of the V_2O_5 sol are studied in the slit-ultramicroscope, it appears that particles oriented in the direction of the incident ray are invisible; on the other hand, particles placed at right angles to the direction of the incident ray, and those that do not deviate from that position by more than 25°, can be observed. Years ago, SIEDENTOPF [22] found that particles which vary considerably in length and breadth can be noticed only when their long dimension is perpendicular (or nearly so) to the direction of illumination.

When dealing with disk-shaped particles, therefore, we shall observe these only in case their maximum cross section is perpendicular, or approximately perpendicular, to the direction of the incident ray. Since these small disks are in constant motion due to the Brownian movement, and topple over once in a while, they will alternately assume favorable and unfavorable positions for observation. In the ultramicroscope this is revealed by a constant scintillation, one and the same particle being alternately light and dark. This peculiar phenomenon is characteristic of disk-shaped particles.

In the beginning, the crystallinity of the particles of the V_2O_5

sol was a subject of controversy. This is not surprising, since at the time of the first observation of this phenomenon the researches of Debye and Scherrer (see p. 134) had not yet been made. Previously, Wiener and Ambronn had shown that small rods, which in themselves were not double-refracting, could give rise to a phenomenon of double refraction when oriented in the same sense in a liquid.

Reinders [24] found later that the peculiarities of the V_2O_5 sol could be reproduced with various other sols, prepared by dispersing suitable inorganic substances of unquestionable crystalline nature with the aid of protective colloids. At present there can be no doubt that all these sols are crystalline. Hence, the phenomenon of double refraction of sols, due to the orientation of the particles must be ascribed to the crystal character of the particles. It occurs whenever at least one dimension is considerably smaller than the other dimensions.

Recent investigations of Freundlich and his pupils [25] have led to a confirmation and extension of these ideas concerning the double refraction of sols. Interesting data have been revealed since Szegvari [26] introduced the asimuth diaphragm in his work. This is a diaphragm in the form of a slit which is placed underneath the cardioid condenser, thus replacing the uniform illumination by a one-sided illumination. It appears that in concentrated V_2O_5 sols there are always present aggregates of parallel particles, a fact which bears a remarkable resemblance to the liquid crystals of Bose's " swarm" theory.[27]

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CHAPTER IX

PROPERTIES OF SUSPENSOIDS FROM THE KINETIC POINT OF VIEW

50. Brownian Movement.—When ZSIGMONDY, in 1904, made the first observation with the ultramicroscope, he was struck by a phenomenon which he describes in the following sentences: [1]

> The small gold particles no longer float, they move—and that with astonishing rapidity. A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold! They hop, dance, jump, dash together, and fly away from each other, so that it is difficult in the whirl to get one's bearings.

Indeed, the phenomenon of Brownian movement, which had first been observed and described in 1827 by the English botanist, ROBERT BROWN,[2] aroused more general interest through ZSIGMONDY's observations than ever before. Nevertheless, BROWN's observations were worthy of serious consideration, as were also the experiments which he performed in connection with this phenomenon and the explanation which he suggested.

BROWN noticed that the pollen of *Clarckia pulchella*, when put into water, showed a continual vibratory motion. Although he thought at first that this was a phenomenon pertaining to life, he convinced himself that any material, provided it is sufficiently finely divided, gives rise to the same erratic motion. Plant residues which for several decades had lain in an herbarium, as well as the coal which they gave on combustion, finely ground amber, and powdered minerals, all showed this peculiar irregular movement. In fact, BROWN describes an amusing experiment in which he pulverized a piece of an Egyptian sphinx and observed the same phenomenon in the undoubtedly lifeless particles thus obtained.

He then made sure that no outside influences affected the phenomenon. This negative proof has been confirmed by widely varying methods in the course of the nineteenth century.[3] The movement is not affected by mechanical vibrations, unequal distribution of heat, the influence of surface tension, or electrical factors; and numerous investigators after Brown have rightly stated that the Brownian movement is a general property of finely divided matter.

However, the motion of the particles, when viewed through the ordinary microscope, never amounts to more than a slow vibration, and hence the phenomenon did not attract much attention on the part of Brown's contemporaries, even after the remarkable development of the kinetic theory of gases in the course of the nineteenth century. What Zsigmondy observed was, however, such a clear picture of molecular motion as conceived by the kinetic gas theory, that after 1903 the interest in the Brownian movement was actively revived both theoretically and from the experimental point of view. In terms of the kinetic theory of gases, the temperature is determined by the kinetic energy of the molecules, i.e., by their $\frac{1}{2}mv^2$, where m is the mass and v the velocity of the particle at that temperature. If the Brownian movement of a colloidal particle is considered as a heat motion corresponding to the temperature of the sol, $\frac{1}{2}mv^2$ must be the same for a molecule of the dispersion medium and for a colloidal particle; they vary considerably in m and for this reason must have correspondingly different values for v at the same temperature. We know the velocity of the molecules from the kinetic theory of gases, and also the size of a visible colloidal particle, as discussed on page 140. Hence, if the *velocity* of the particle were known, the size of the molecule would be the only remaining unknown and could be calculated from the other data.

Our first thought, then, would be to reproduce by means of a drawing apparatus the path of a particle, measure it, and compute the velocity from these measurements. Attempts to arrive at the size of the molecules in this manner failed,[4] as we now realize, for obvious reasons. If we calculate how many collisions a colloidal particle of even comparatively *large* dimensions suffers, we arrive at the conclusion that a gamboge particle of, say, 400 mμ diameter, at 17°, changes its direction by an angle of 90° thirty million times per second.[5] Hence, it is absolutely impossible to follow the path of a particle with the eye or by means of a moving picture apparatus. What is supposed to represent the course of the particle is in reality only a very crude image of it.

Since the possibility of measuring the velocity of the particle appears to be excluded, an entirely different line of attack is necessary to solve the problem. What we can determine is the rectilinear displacement of a particle in unit time. EINSTEIN,[6] and, almost simultaneously, VON SMOLUCHOWSKI [7] have calculated, on the basis of probability considerations, what the average displacement of a particle must be. They obtain the following value for the mean displacement, $\overline{\Delta}_x$, in the direction of a horizontal axis, x:

$$\overline{\Delta}_x = \sqrt{t}\sqrt{\frac{RT}{N}\cdot\frac{1}{3\pi\eta r}},$$

where R is the gas constant, T the absolute temperature, N the constant of AVOGADRO, η the viscosity of the medium, and r the radius of the particle. In this expression we recognize the quantity $\frac{RT}{N}$, which is connected with the kinetic energy of the particle, and the expression $6\pi\eta r$, which in STOKES' law denotes the ratio of the velocity to the force of friction for a particle moving in a liquid.

Different investigators [8] have chosen this theory as a foundation for their experiments, since it opened, for the first time, a way to determine the highly important factor N, AVOGADRO'S constant. We shall devote our attention especially to the work of PERRIN.[9]

PERRIN employed, in all his experiments, disperse systems of gamboge and mastic. These were very carefully prepared and were separated by fractional centrifuging into systems having particles of uniform size. The sizes ranged between 0.212 and 11.5 μ.

These particles are visible in the ordinary microscope. Their size was determined by direct measurement either from the rate of fall, according to STOKES' law, or else by counting. The path of a particle was sketched on cross-section paper by indicating its position after equal intervals of time. In different series of measurements this period was either 30, 60, 90, or more seconds. By carrying out a large number of measurements PERRIN succeeded in estimating the average displacement during the stated period of time. By calculating by means of EINSTEIN's formula the constant N, he obtained the results given in Table XXII.

TABLE XXII

Material	Radius of the particle	N
Gamboge.....	0.50 μ	66×10^{22}
	0.212	73×10^{22}
Mastic.......	5.50	78×10^{22}
	0.52	72.5×10^{22}
	0.367	69×10^{22}

This table shows that the values for N found in the various determinations fluctuate somewhat, but we can infer from these data that N is independent of the size of the particles. This result is extremely important when it is remembered that a particle with a radius of 5.5 μ is 17,000 times larger than one with a radius of 0.212 μ. PERRIN rightly considered this result a strong confirmation of the kinetic theory of gases. In fact, the trend of thought here developed is applicable to systems of such variety of sizes that extrapolation to particles with molecular dimensions seems justified.

Hence, the kinetic theory of gases holds, irrespective of the size of the particle under consideration; in other words, the mean kinetic energy of all particles is alike at the same temperature. This conclusion considerably broadens our knowledge of the properties of colloids.

Modern investigations, in which other methods were employed, have shown that the most accurate value for N is 60.6×10^{22}.

51. Diffusion.—The speed of diffusion is governed by the law of FICK, which is expressed in the equation:

$$dm = Dq\frac{dc}{dx}dt,$$

where dm is the quantity of matter which in the time dt moves through the cross section q when the concentration gradient on either side of that cross section is equal to $\frac{dc}{dx}$. The diffusion constant, D, is, therefore, the quantity of matter which in unit time moves through the unit of cross section for a difference in concentration equal to unity. Einstein[10] noticed that this diffusion constant is closely related to the displacement, $\overline{\Delta}_x$, discussed in Sec. 50, in such a way that:

$$D = \frac{\overline{\Delta_x}^2}{2t};\ \text{hence, } D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}.$$

Svedberg[11] checked this equation and confirmed it in his experiments with gold sols. Here too, it appears that colloidal particles behave like large molecules.

In an entirely different way, Perrin[12] applied this idea with the aid of the previously mentioned disperse systems of mastic and gamboge. Perrin reasons as follows: Let us consider a liquid column of such an emulsion. Any particle that consists of matter of greater density than water is pulled down by the force of gravity; its Brownian movement, i.e., its tendency to diffuse, has an upward component which tries to balance the tendency to fall. The final result is that after a while the particles distribute themselves in such a way that the concentration at the bottom of the column is quite large, that at the top very small, and intermediate values occur between top and bottom.

The quantitative relations may be represented as follows: We are dealing with a system containing n particles per unit volume. The tendency to diffuse upward can be expressed numerically by the "osmotic pressure," as derived from the theory of dilute solutions. The latter is equal to $n\frac{RT}{N}$. Let us next consider two levels in the column of liquid at heights h and $h + dh$ from the base. When these layers have reached equilibrium the number of particles in each is n and $n + dn$, respectively. The diffusion tendency in these layers is $n\frac{RT}{N}$ and $(n + dn)\frac{RT}{N}$, so that a difference of $-dn\frac{RT}{N}$ in diffusion tendency exists.

The influence of the gravitational force is governed by the quantity $\phi(d_a - d_{H_2O})$, where ϕ is the volume of the particle, d_a its density, and d_{H_2O} the density of water. Equating these two forces which balance each other, we obtain:

$$-\,dn\frac{RT}{N} = n\phi(d_a - d_{H_2O})g\,dh,$$

which may be written in the form:

$$-\frac{dn}{n}\frac{RT}{N} = \phi(d_a - d_{H_2O})g\,dh.$$

We can integrate this expression between n_1 and n_2 at the respective heights h_1 and h_2 and obtain:

$$\frac{RT}{N}\,ln\frac{n_2}{n_1} = \phi(d_a - d_{H_2O})g(h_1 - h_2). \quad . \quad (1)$$

PERRIN placed his mastic emulsion under the microscope and focussed the latter at different heights, each time counting the number of particles. In this manner he obtained the numerical results given in Table XXIII. One series of his experiments is graphically represented in Fig. 75. If the number of particles at the height $h = 5\,\mu$ is arbitrarily fixed at 100, one notes at the other heights corresponding figures, as found (Column 2, Table XXIII) and as calculated (Column 3). The agreement is quite remarkable.

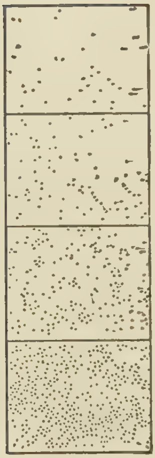

FIG. 75.

TABLE XXIII

Height in μ	Number found	Number computed
5	100	100
15	43	45
25	22	21
35	10	9.4

The formula derived and the discussion leading to it are similar to that which is used for finding an expression for the density of the atmosphere, viz.:

$$ln\frac{p_1}{p_2} = k(h_1 - h_2).$$

It is interesting to note that 6 kilometers in the atmosphere of the earth are equal to 10 μ in the mastic sol!

Burton,[13] as well as Porter and Hedges,[14] has pointed out, however, that Perrin's formula cannot possibly apply to colloid systems in general. Writing formula (1) in the form:

$$ln\frac{n_2}{n_1} = K(h_1 - h_2),$$

where $K = \frac{N}{RT} \cdot \phi(d_d - d_{H_2O})g$, we find, on substituting the values for a silver sol, $K = 5000$. This would mean that the concentration of silver in a silver sol at a given layer is 5000 times that of a layer 1 cm. higher than the first! This result conflicts flagrantly with the experience of any chemist who has ever worked with gold or silver sols. Strange to say, Westgren's results were in complete accord with the equation of Perrin over a depth of 1.1 mm.

Porter and Hedges state that the formula of Perrin assumes the validity of the law of Boyle, while the computations show that the volume of the particles plays a large part. Taking this factor into account, one finds an expression of different form. This is well shown in the accompanying diagram, Fig. 76, where both Porter's and Perrin's curves (the latter dotted) are drawn. It is seen that they coincide for a small difference in level, but deviate considerably for greater differences. There is still considerable difference of opinion concerning the correct interpretation of the deviations from the theory of Perrin.[15]

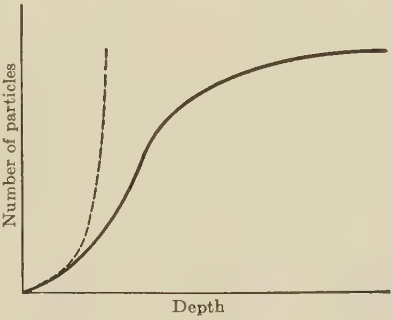

Fig. 76.

52. Osmosis.—Osmosis may be regarded as diffusion interrupted from one side only. When water and a sugar solution are in contact with each other, the sugar molecules move in the direction of the water, and the water molecules, conversely, migrate in the direction of the sugar solution, since the concentration gradient for these molecules is negative in the directions indicated. If the two are separated by a wall that allows the passage of the water, but not of the sugar solution, only the water molecules move; hence, the osmotic phenomenon is the result of the one-sided flow of water. The osmotic pressure that compensates for this phenomenon is a pressure that forces through the membrane, in the direction of the water, a number of water molecules equal to that which, by diffusion, would enter the sugar solution.

The magnitude of this osmotic pressure is determined by the number of kinetically active particles present in one liter of the solution, according to the law of VAN'T HOFF:

$$\pi = RT\frac{n}{V},$$

where n is the number of particles and V the volume of the solution. From the preceding discussion, it is clear that the size of the particles in the solution is immaterial; what does matter is the number present per liter. VAN'T HOFF'S law indicates that when one gram-molecule, i.e., 60.6×10^{22} particles, is present in one liter at 0° the osmotic pressure will be 22.4 atmospheres. This rule can be directly applied to colloids.

If, however, one calculates what this pressure must be for a colloidal solution, the conclusion is readily reached that it hardly exceeds the limit of perceptibility.

Let us imagine, for instance, a gold sol with particles having a mean diameter of 4 mμ. If we work with round numbers, a sol having 1 g. of gold per liter contains 50 cu. mm. of gold, while the volume of each particle is about 50 cu. mμ. One liter of the sol contains, therefore, 10^{18} particles of gold. If a sol with 60.6×10^{22} particles is called a "normal solution," this sol is 0.000002 normal, and its osmotic pressure amounts to $\frac{1}{2}$ mm. of water, corresponding to a lowering of the freezing point equal to 0.000004°.

It is obvious that colloidal solutions will show no measurable osmotic pressure, no depression of the vapor pressure, no lowering of the freezing point, and no rise of the boiling point. This corresponds, in general, with the known facts.

Nevertheless, it is not an easy task to confirm this inference experimentally with complete certainty. As a matter of fact, colloidal solutions always contain a certain amount of peptizing electrolyte (*cf.* p. 86) which is partly adsorbed by the particles but also occurs in adsorption equilibrium in the intermicellar liquid. The liquid system is, therefore, never a sol alone but at the same time a true solution. In the determination of the lowering of vapor pressure, the rise of boiling point, and the depression of freezing point, the substances in true solution must of necessity complicate the phenomenon. An attempt has been made, in measuring osmotic pressures, to eliminate the influence of any electrolytes that may be present in the sol, by selecting an osmotic membrane that is pervious to substances in true solution but impermeable to colloidal substances. These properties, as we have seen, are characteristic of parchment paper, fish bladder, and collodion, the so-called dialysis membranes. It is to be expected that further elimination of the influence of substances in true solution could be effected by measuring the osmotic pressure not with respect to water but with respect to the intermicellar liquid. Hence, the osmotic phenomenon has been measured against the ultrafiltrate (*cf.* Sec. 54 of this chapter).

This method of procedure is based on the idea that substances in true solution, under the conditions just described, do not participate in the osmotic equilibrium. However acceptable this may appear at first sight, DONNAN'S theory, which will be discussed on page 219, shows that even under these circumstances a direct measurement of the osmotic pressure does not permit conclusions, based on the law of VAN'T HOFF, regarding the number of colloidal particles that might cause the osmotic phenomenon.

Moreover, the greater the accuracy and the care with which the osmotic measurements are carried out, the more closely the final value approaches zero, in agreement with the reasoning given at the beginning of this section.

53. Dialysis.—On page 9 reference was made to dialysis. In connection with what was said in Sec. 52 it is clear that we can dialyze without any appreciable excess pressure only because the osmotic pressure of the colloidal particles approaches the value of zero so closely. As a matter of fact, there is no fundamental difference between a dialyzer and an osmotic cell in which colloidal systems are measured.

Nevertheless, in dialyzing, the impression is often gained that colloidal solutions exhibit quite a noticeable osmotic pressure; frequently the liquid inside the dialyzer rises considerably, especially during the first period of the dialysis. There is no doubt that we can look upon this process as an osmotic phenomenon; but it is not an *equilibrium* phenomenon, as required by the law of VAN'T HOFF. It is caused by the fact that substances in true solution, although capable of passing through the membrane, nevertheless encounter a considerable resistance as compared with water. Hence the inflow of water exceeds the total outflow of water and electrolytes. Owing to the resulting excess pressure, the counter current is reinforced and hence the phenomenon becomes less pronounced after a while.

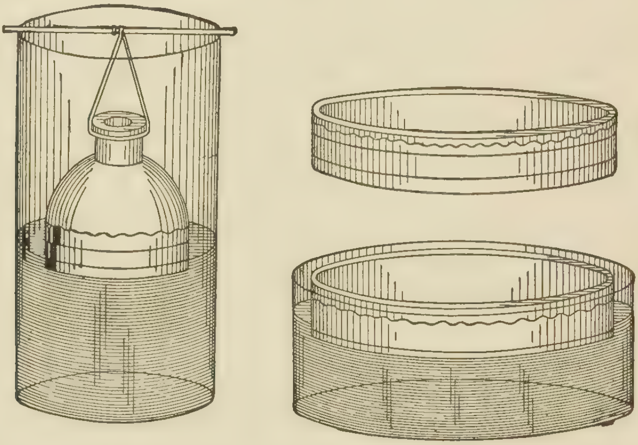

FIG. 77.

Parchment paper is the classic material, extensively used by GRAHAM in various forms (see Figs. 1 and 77). It is put on the market in different shapes, which have certain advantages in dialyzing: thimbles consisting of one piece (SCHLEICHER and SCHÜLL, Fig. 78); and long tubes which are sealed by means of some colloidal paste (DESAGA). These U-shaped tubes are filled with the liquid to be dialyzed and are placed in water, which is continually renewed (Fig. 79). This procedure can be reversed by allowing the water to run through the tube while the colloid is in the outside vessel. In this way the process can also be carried out at higher temperatures, to insure rapid dialysis.[16]

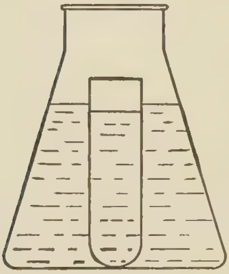

FIG. 78.

Even so, parchment paper is a slow dialyzing material; it offers considerable resistance to water as well as to electrolytes. Moreover, it is not always easy to obtain fairly large sheets of parchment paper free from small holes. Fish bladder and various amnion membranes are to be preferred. Collodion membranes are most widely employed since they are easy to make and permit an exceedingly rapid dialysis.

A 6 per cent collodion solution, as used in photography for wet plates, can be poured into any desired shape. When this is immersed in water, both alcohol and ether are displaced by water and a membrane of sufficient strength is obtained. Thimbles are made by pouring the collodion solution over the outside of a test tube or else, by covering the inside of a beaker or flask with the liquid. When the greater part of the alcohol and ether has evaporated the remaining film is covered with water and can be loosened from the glass wall. The permeability of collodion membranes depends to a large extent on the time allowed for vaporization of the solvent previous to the soaking of the film in water.[17] It is also feasible to soak filter-paper thimbles, such as those used for the Soxhlet apparatus, with the collodion solution, and thus prepare durable dialysis thimbles.

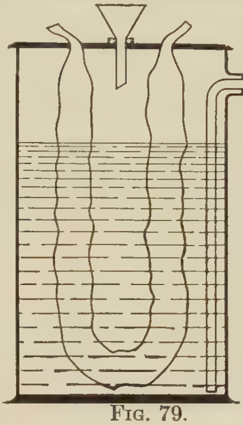

Fig. 79.

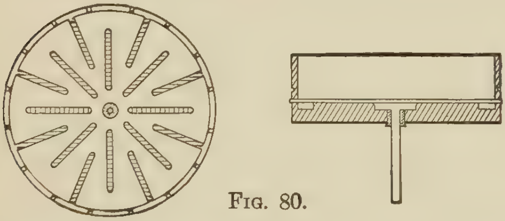

Fig. 80.

It is, of course, necessary to have as much clean water on the outside of the membrane as is possible. This means that the outside water has to be frequently renewed in order to obtain the highest possible concentration gradient. Zsigmondy and Heyer[18] have constructed a dialyzer which satisfies the severest requirements (Fig. 80). A collodion membrane is attached to an ebonite ring. This dialyzer is then placed on top of a star-shaped chamber so that the outside water is only present as a thin column of liquid which can be continually renewed without using too great quantities of distilled water. On account of the peculiar shape of the dialyzing chamber, the instrument is called a " star-dialyzer."

A method has been devised to increase the dialyzing effect so that the time is shortened. This is the process of *electro-dialysis*, a combination of dialysis and electric transport. The principle is illustrated in Fig. 81. The instrument consists of three compartments, the second of which contains the colloidal solution. The two outer cells are separated from the middle one by two dialysis membranes, M_1 and M_2; two electrodes, E_1 and E_2 are inserted in these chambers while fresh water is introduced continually. The electric current carries the electrolytes into the outer compartments. The effect is further increased by the special preparation of the membranes.[19]

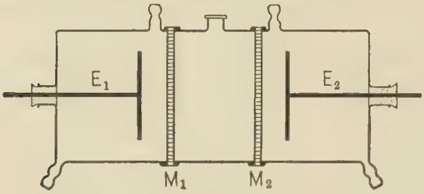

FIG. 81.

54. Ultrafiltration.—Dialysis is still at best a comparatively slow process. In order to deprive a sol quickly of its intermicellar liquid, we can accelerate the dialysis phenomenon by forcing the intermicellar liquid through the membrane under pressure. This process is known as ultrafiltration. The membranes employed are made from collodion dissolved in glacial acetic acid or in alcohol-ether.

This forced dialysis, or osmosis (depending on the point of view), is sometimes useful for preparatory purposes. On page 112 we saw, for instance, that such a separation of the intermicellar liquid serves a definite purpose. It has been wrongly assumed, however, that ultrafiltration in itself affords a means of determining the size of the particles. By choosing different concentrations of collodion solution, membranes of different degrees of permeability are obtained, and this has been considered to be due to different degrees of porosity of the membranes, the latter acting as sieves.

This assumption, however, appears to be largely incorrect. Filter and membrane action is only to a limited extent comparable with the action of a sieve, and is much more dependent on the adsorption at the capillary wall than on the mechanical dimensions of the pores. For instance, a positively charged colloid cannot be filtered through a negatively charged filter paper, when the latter is rather thick; a negative sol, however, passes through easily. This question will be reconsidered later. BECHHOLD[20] has reported a close connection between the concentration of his membranes and the size of the particles held back by them, but this fact in itself does not prove anything regarding the sieve mechanism of the ultrafilter. It is also possible that the adsorbability runs parallel with the particle size. If we could consider substances that are comparable as regards their adsorbability and their electro-adsorbability, a direct connection between the size of the particles and the nature of the ultrafilters might add something to our knowledge of the size of the particles; but a comparison of completely dissimilar substances, on the basis of their behavior toward ultrafilters, does not permit any conclusion regarding the size of the particles.

Ultrafiltration, therefore, is exclusively a useful experimental process. It cannot furnish a direct method for studying particular properties of a sol.

The theory regarding the nature of the dialysis membrane has been strengthened by experiments of W. Biltz [21] on the permeability of collodion membranes for aniline dyes. He arrived at the conclusion that the permeability of such a membrane depends on the number of atoms present in the molecule of the dye. If the number is less than 45, the dye passes the membrane readily; for a number exceeding 45, the permeability decreases rapidly; while it is practically *nil* for dyes containing between 55 and 70 atoms per molecule. For molecules with more than 70 atoms, the membrane is absolutely impervious.

At first sight it might be thought that the mechanical dimensions of the molecule really do determine the permeability, but further results of Biltz do not confirm this inference. The limits just mentioned are raised when sulpho-groups occur in the molecule, and they are lowered when alizarine-groups are present. The size of the molecule, therefore, is not in itself a measure of its diffusibility. Evidently, the phenomenon is governed by physico-chemical properties which run more or less parallel with the size of the molecule but depend also on its constitutive properties. In dealing with adsorption we also saw that the adsorbability increases with the size of the molecule but is furthermore dependent on its constitution.

The various methods of ultrafiltration differ only in the manner in which the collodion membrane that is used in filtering acquires the proper strength to withstand the pressure necessary for the acceleration of the speed of filtration. Wo. OSTWALD [22] prepares wet filter paper in such a way that fine collodion coatings are formed in the pores. These so-called spontaneous filters allow a rapid filtration under exceedingly small pressures. ZSIGMONDY [23] places the collodion film on a suitable porcelain sieve bottom. BECHHOLD,[24] using unglazed porcelain as a support, has constructed a number of very convenient devices for the same purpose.

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CHAPTER X

FORMATION OF SUSPENSOID SOLS

55. General Classification.—Up to the present we have paid little attention to the formation of suspensoids. SVEDBERG in his handbook "Herstellung kolloider Lösungen anorganischer Stoffe"[1] (*cf.* "Formation of Colloids," by the same author), has indicated a general principle by stating that a system containing colloidal particles can, as a rule, be prepared in two different ways: by condensing a highly dispersed system, or by dispersing a coarse dispersed material. As an example of the first method, we may mention the preparation of a gold sol as described below. We start with a solution of gold chloride, in which the gold is molecularly, or rather ionically, dispersed. By reduction, the gold chloride is transformed into gold, and the gold atoms then unite to form smaller or larger gold particles; hence this sol is made by the *condensation* method.

As an example of the *dispersion* method, we may imagine some coarse material which is ground under water to such a fine state of subdivision that colloidal dimensions are attained, while at the same time the newly formed system remains stable.

This general classification of SVEDBERG has been well chosen and is very useful, provided we realize that there are a number of transitional cases. This consideration, however, cannot prejudice us against the system, since in any system we must always discriminate sharply between different concepts.

A well-known method for preparing metal sols consists in establishing an arc between two metallic wires immersed in water. Colloidal dispersion of the metal takes place. It is reasonable to consider this a dispersion method because the coarse material of the electrode is dispersed into a fine colloidal sol. It should be kept in mind, however, that the metal is vaporized in the electric arc and then undergoes condensation, which means that a condensation method is in reality involved.

Other transitional cases will be referred to later.

56. Condensation Methods.—Before taking up SVEDBERG'S systematic classification of condensation methods, we shall first of all consider what may happen and then see what actually does happen in a condensation method. When the molecularly dispersed material is transformed by a chemical reaction into a material capable of forming particles which are insoluble or difficultly soluble in water, it is to be assumed that at one particular stage the material is present in a molecularly dispersed state. For instance, when molecules of $AuCl_3$ are being reduced to gold atoms, at a certain moment there is present a "supersaturated" solution of gold in water. From this supersaturated solution the gold particles crystallize, forming the sol.

The formation of such a new solid phase from a liquid system has in late years been a frequent subject of investigation. TAMMANN[2] and his pupils, in particular, have studied the crystallization from the molten state: Their researches have shown that this process must be differentiated into two parts, viz., *the formation of nuclei* and *the velocity of crystallization.* A nucleus, once formed, grows at a certain rate, at the expense of the material still in molecular dispersion. The first part of the process, however, is the union of atoms to form a nucleus.

The formation of nuclei increases at temperatures below the melting point of the substance under investigation. Fig. 82 gives an idea of the nucleus formation in molten betol. It is seen that below the melting point, T_0, the number of nuclei first increases, then attains a maximum, and finally decreases. The shape of the curve suggests immediately the idea that the phenomenon is governed by probability. It has often been assumed that only atoms with a velocity higher than the average unite to form nuclei. It is more likely, however, that deviations from the uniform distribution give rise to nucleus formation. At any location where a large number of atoms are close together in a

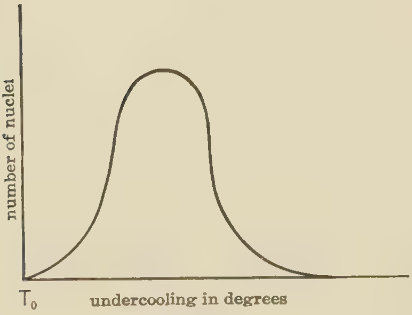

FIG. 82.

configuration resembling somewhat a crystal lattice, a crystal nucleus is produced.

Experiments by TAMMANN have, furthermore, proved that additional material, either heterogeneous or homogeneous, that may be present, furthers the formation of nuclei in some cases and hampers it in others.

Figure 83 shows how the *rate* of crystallization of a given crystal changes with the temperature. At the melting point, T_0, it is, of course, zero; but below that point it first increases rapidly, then remains constant over a certain range of temperatures, and at a still lower temperature falls off rapidly.

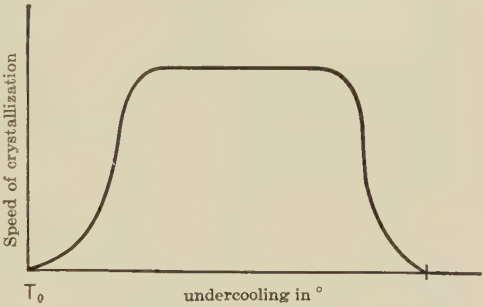

FIG. 83.

The course of the crystallization of a substance from its melt is, therefore, governed (1) by the number of nuclei formed and (2) by the speed with which these nuclei grow.

Regarding the crystallization from supersaturated solutions, we have at our disposal the researches of MARC and his co-workers.[3] The speed of crystallization appears to be largely dependent on the degree of supersaturation and on the presence of added substances, especially when the latter are adsorbed by the surface of the crystal (or by the nucleus).

It is evident that in the case of suspensoids the problem of nucleus formation and rate of crystallization dominates the whole process. When only a small number of nuclei are formed and these grow rapidly, no colloidal systems can be produced, because these few nuclei rapidly become large particles. If, on the other hand, a large number of nuclei are formed and their rate of crystallization is slow, the conditions for the formation of a colloidal solution are favorable, *provided electrical conditions are likewise suitable.* For, as we have seen in preceding chapters, the electric charge completely governs the stability of suspensoids.

In the method discussed on page 141, where a solution containing nuclei is added to the gold sol in the course of preparation, an artificial formation of nuclei is brought about, and the size of the particles from this time on is dependent only on the speed of crystallization. Such a manipulation can, of course, be applied only when the spontaneous formation of nuclei is so small that the number of nuclei may be considered as determined entirely by the concentration of the added nucleus solution.

Following SVEDBERG'S classification, we may group the different condensation methods according to the chemical reactions which take part in their formation. We then obtain the following classes of methods:

(*a*) *Reduction methods.*—Nearly all sols of metals are prepared in this manner. Numerous reducing agents may be employed. Using pure hydrogen, we can reduce, for instance, silver oxide according to the equation:

$$Ag_2O + H_2 = 2Ag + H_2O.$$

Silver oxide is brought into contact with water through which is passed a stream of hydrogen gas. Insofar as the oxide is dissolved, it is, obviously, reduced, and the silver atoms unite to form colloidal particles. The silver oxide is continually dissolved and then reduced. It is evident that the sol thus formed is *poly-disperse* (containing particles of different size, as contrasted with an *iso-disperse* sol having particles of the same size) because the reduced silver oxide finds more and more nuclei. Viewed in the ultramicroscope, this sol presents a very colorful picture which reveals the poly-dispersity very plainly.

Phosphorus has long been used as a means of preparing gold sols:

$$AuCl_3 + 3H_2O + P = Au + P(OH)_3 + 3HCl.$$

Experience has shown that this method is a slow process for making highly dispersed amicroscopic gold sols. These sols are used as nucleus solutions for the preparations discussed in Sec. 48.

Ordinarily, formaldehyde or H_2O_2 is used, with the addition of a little alkali, often in the form of K_2CO_3. The presence of OH ions is obviously required in order to bring about suitable electrical conditions.

Selenious acid can be reduced to colloidal selenium by means of either sulphur dioxide or hydrazine:

$$SeO_2 + 2SO_2 = Se + 2SO_3.$$

(*b*) *Oxidation methods.*—Colloidal sulphur is prepared by the oxidation of H_2S by means of SO_2, as expressed in the following reaction:

$$2H_2S + SO_2 = 3S + 2H_2O.$$

The sulphur separates in colloidal form. The process is, however, more complicated than would appear from the above equation. In this so-called WACKENRODER liquid, polythionic acids are formed simultaneously with the sulphur (*cf.* p. 260).

(*c*) *Hydrolysis methods.*—Numerous metallic oxides are insoluble in water and form colloidal oxides when their salts are hydrolyzed. Sols of the oxides of chromium, iron, aluminium, tin, and other metals are prepared by simply dialyzing the salts, dissolved in water, against water. When nitrates are used, nitric acid passes through the dialyzer and leaves a colloidal solution of the oxides behind.

(*d*) *Other decompositions.*—The sols of the oxides just mentioned can also be prepared by means of the following double decomposition:

$$2FeCl_3 + 3(NH_4)_2CO_3 = 6NH_4Cl + \underbrace{Fe_2(CO_3)_3}_{Fe_2O_3 + 3CO_2}$$

The formation of sulphide sols likewise belongs to this group; for instance:

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

It is evident, however, that not every reaction is suitable for such a preparation of sols, for the reason that we operate here with electrolytes which might flocculate the colloidal particles eventually formed. Too great a concentration of electrolyte is therefore inadmissible, both at the beginning and at the end of the reaction. The second reaction just mentioned is, of course, eminently satisfactory as far as the final product is concerned, H_2O being formed. Hydrogen sulphide is only slightly soluble in water and is, moreover, removed at the end by passing hydrogen gas through the sol. To prevent the possibility of having too much As_2O_3 in the solution at the start, a solution of As_2O_3 is allowed to drop into water through which a stream of hydrogen sulphide passes. The electrolyte is then added in small quantities and rendered harmless by its transition into colloidal material.

The preparation of silver halides, discussed on page 110, also belongs to this group. It was previously stated that the maintenance of proper electrical conditions is necessary for the formation of these sols. The fact that the conditions are not the same for different halides is due to individual differences in speed of crystallization and in nucleus formation, and possibly also to differences in the boundary potentials of these halides with respect to the liquids used.

(*e*) *Reduction of solubility.*—A fifth method is that which makes use of the decrease in solubility, substituting water as a solvent for an organic medium. For instance, when sulphur crystals are dissolved in alcohol, a true, molecularly dispersed solution is formed. As soon as this solution is poured into water (in which solvent the sulphur is practically insoluble) the sulphur condenses to colloidal particles. The alcohol which remains dissolved in the water can be removed by dialysis. In the same manner we can make mastic sols or hydrosols of various organic substances. First, however, it may be necessary to produce conditions suitable for colloid formation by introducing peptizing agents into the water in order to stop the condensation at the point where particles of colloidal dimensions are built.

57. Dispersion Methods.—Four different methods may be grouped under this heading:

(*a*) *Mechanical subdivision.*—When the substance has been so finely ground in a mill that the diameter of the particle is reduced to less than 1 μ, the conditions are suitable for sol formation. In the past few years, several " colloid mills " have been put on the market. However, an extremely fine subdivision is not sufficient to produce a stable sol. For this reason a peptizer (often wrongly called a " disperser " or " dispergator ") is always introduced into these mills. Very often this peptizer is purely a protective colloid. (*Cf.* Sec. 31 *b.*)

In case no mechanical subdivision takes place and yet the method of preparation is one of dispersion, the inference is that primary particles of colloidal dimensions were originally present. The procedure which is followed in peptizing an agglomeration of such primary particles is exemplified in the next two methods:

(*b*) *Washing-out method.*—In case too much electrolyte is present in the preparation of a colloid by the method of double decomposition, a precipitate is often formed, which in its turn can be brought back to the state of colloidal solution by washing out the excess of electrolyte. This occurs frequently in analytical chemistry with those precipitates which, on washing, " run through the filter." For instance, when vanadium pentoxide is precipitated in the reaction:

$$2NH_4VO_3 + 2HCl = V_2O_5 + 2NH_4Cl + H_2O,$$

there is obtained a reddish-brown precipitate which can be filtered. When water is poured over this precipitate, a clear filtrate containing NH_4Cl runs through at the start. After a while the filtrate becomes reddish-brown and a colloidal solution of V_2O_5 is obtained.

(c) *Peptization methods.*—It often happens that precipitates consisting of fine primary particles need only to have their boundary potentials raised by means of a peptizing electrolyte in order to go into colloidal solution (*cf.* Ch. VI). When hydrogen sulphide is passed into a solution of corrosive sublimate, HgS precipitates. If the hydrochloric acid which has been formed is then removed by rinsing repeatedly with water, a colloidal black solution of HgS can be obtained by peptizing the precipitate with H_2S.

Precipitated Fe_2O_3 can be peptized by the addition of $FeCl_3$, a method which is easily understood from the discussion on page 107.

From the cases mentioned under *b* and *c*, it is evident that we are dealing here with a flocculation that is not quite irreversible. If it were absolutely irreversible, neither the washing away of the electrolyte that is present nor the addition of a peptizing electrolyte could possibly give rise to the formation of a sol; hence, only a limited number of cases are adapted to these two methods.

(d) *Electrical disintegration.*—Bredig[4] has prepared collodial systems of gold, silver, and platinum by establishing, in water, a direct current arc between electrodes composed of these metals. Svedberg[5] has extended this method by using alternating current, since direct current causes a considerable amount of charring when the disintegration takes place in organic liquids. In this way, Svedberg was able to disperse the lighter metals, which readily react with water when in a finely divided state, by employing organic liquids (preferably isobutyl alcohol or ether). He even obtained colloidal solutions of such metals as potassium and sodium.

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CHAPTER XI

HISTORICAL OUTLINE OF THE DEVELOPMENT OF THE THEORY OF SUSPENSOIDS

58. Introduction.—The preceding chapters presented a sketch of the theory of suspensoids that seems, at the present time, to give the best insight into the behavior of these systems. Nobody can be blind to the fact that current opinions are far from adequate. The more the investigations considered are extended and applied to other suspensoid sols, the better one realizes that the picture drawn has been highly idealized. An extension of the theory presented, possibly a radical improvement, may be expected. After all, any theory in the domain of the natural sciences is based on the conception of facts that prevails at a certain period, only to be succeeded by another which presents a better and truer correlation. It is wise, therefore, to consider a theory merely as a link in the long chain of consecutive interpretations of scientific facts; consequently, this chapter is devoted to a brief historical sketch of previous experiences and theories which have led to modern conceptions regarding suspensoids.

59. The Nineteenth Century.—GRAHAM is often regarded as the first systematic investigator of colloidal systems, although it is undoubtedly more correct to give first mention to FRANCESCO SELMI, of Modena, whose publications, written in Italian, have recently become accessible in an English translation.[1] SELMI realized, as early as 1845, that a colloidal solution of AgCl differs radically from a true solution, and extended this idea in the following years to sols of Prussian blue and sulphur. He was struck by the ready precipitation of these substances by various neutral salts which, nevertheless, do not react in a chemical sense, and by the absence of a heat effect and volume change at the flocculation point; hence, colloidal systems were considered by SELMI as pseudo-solutions.

GRAHAM[2] deserves special credit for his exhaustive study of the physical properties of colloidal solutions, more particularly of their diffusibility. The slight diffusion of colloids leads to the assumption that the diffusing particles are much larger than molecules, which are truly dissolved. This diffusion furnishes a characteristic criterion by which to distinguish between true solutions and colloidal solutions. GRAHAM was wrong, however, in considering the power to form colloidal solutions a specific property of certain compounds instead of a general property of matter.

NÄGELI [3] vigorously advocated the theory of the polymolecularity of colloidal particles, for which he used the term *micells*. A peculiar position in the development of colloid chemistry and the theory of adsorption is that assumed by J. M. VAN BEMMELEN,[4] who studied a number of agricultural problems, especially the interaction of precipitated colloids with water and salt solutions. This experience enabled him to collect a wealth of most valuable data (see Chapter XVI) and to prepare the way for the modern theory of adsorption. Theoretically, he arrived at a negative, though highly important conclusion, viz., that the union of water and other substances with colloids is *not stoichiometric*.

Around 1880, the first systematic investigations concerning flocculation were published. The flocculation of As_2S_3 and Sb_2S_3 by countless electrolytes was studied first by SCHULZE,[5] and later, in much greater detail by LINDER and PICTON.[6] The predominating rôle of the ion carrying a charge of opposite sign, and of the valence of that ion, was clearly brought to the fore, particularly by the last-mentioned workers, who introduced cataphoresis as a new method of attack.[7]

The problems arising in connection with the mechanism of flocculation brought forth a great variety of interpretations in the second half of the nineteenth century. As early as 1851, SCHEERER [8] expressed the opinion that salts decreased the viscosity of the medium, and THOULET [9] thought that the particles became heavier by accumulating the salt in their surface. Both workers assumed, therefore, that flocculation was simply an accelerated sedimentation. But the results of SCHULZE and those of LINDER and PICTON, together with the work of BARUS and SCHNEIDER,[10] clearly demonstrated, in the light of the ionic theory evolved by ARRHENIUS, that certain properties of electrolytes (more particularly the valence) play an important part in the flocculation.

W. B. Hardy,[11] however, was the first to recognize the relation between charge and stability (*cf.* p. 68). Even at present, there is no agreement as to the cause of this relationship. Stark [12] put forth the theory that the non-sedimentation of colloidal solutions was caused by air bubbles adhering to the particles, the adhesion being destroyed by added electrolytes. This theory was proved to be untenable by the work of Bredig and Coehn.[13] The former of these two investigators [14] sought to establish a close connection between what takes place in a capillary electrometer and the coagulation of a colloid. As pointed out on page 51, this instrument shows that the surface tension is high in the absence of an electric charge and decreases when a charge is introduced. The fundamental problem of colloid chemistry is just this (*cf.* p. 11): Why is the surface tension unable to unite the particles? Bredig interpreted Hardy's conclusions by assuming that the surface tension of the charged particles is small and consequently leaves them in a relatively stable condition. The electrolytes, according to Bredig, remove the charge, thereby increasing the boundary tension and thus bringing about coalescence of the particles, followed by flocculation. This concept was undoubtedly a step forward, although it was found later (Ellis [15]) that, even in the case of liquid particles (oil emulsions), the cause of the coagulation does not lie in increased surface tension. The fact remains, nevertheless, that Bredig was the first to look for a rational physico-chemical explanation.

At the same time a search was made for a quantitative expression for the coagulating power of electrolytes. Whetham [16] reasoned as follows: If discharge requires the presence of ions of opposite charge in the vicinity of the particle, there must be present simultaneously 2 trivalent, 3 divalent, or 6 monovalent ions. Since the probabilities for simultaneous presence are proportional to the corresponding powers of the concentrations, Whetham arrived at the following formula for the flocculating concentrations of monovalent, divalent and trivalent ions, c_1, c_2 and c_3:

$$\frac{1}{c_1} : \frac{1}{c_2} : \frac{1}{c_3} = 1 : x : x^2.$$

For $x = 32$, these ratios are as 1 : 32 : 1024, a result which corresponds to the data obtained by SCHULZE and by LINDER and PICTON for the As_2S_3 sol.

In those years, around the turn of the century, scientists were fairly well convinced that colloidal solutions were micro-heterogeneous systems consisting of suspended polymolecular particles. FARADAY [17] had already proclaimed that gold sols contain gold particles, and yet SCHULZE was not convinced of the inhomogeneity of his sols. On the basis of experiments performed by SPRING [18] and LOBRY DE BRUYN [19] around the year 1900, the TYNDALL effect seemed to furnish a rather doubtful indication in that direction. The proof of the heterogeneity supplied by the ultramicroscope put colloid chemistry on a solid foundation which had hitherto been absent.

60. The First Decade of the Twentieth Century.—The relation between charge and stability formulated by HARDY formed the basis for the dynamics of colloids, and the heterogeneity definitely demonstrated by the ultramicroscope firmly established their statics.

BURTON [20] removed all doubt [21] concerning the correctness of HARDY'S principle. FREUNDLICH [22] confirmed the real significance of the valence and commenced his studies on adsorption [23] in order to understand the mechanism of flocculation. A critical study of the available literature on adsorption had just then been compiled by WI. OSTWALD,[24] and FREUNDLICH was thus able to show the close connection between adsorption phenomena and colloid stability. A few years earlier, PERRIN [25] published the first comprehensive study of electro-endosmosis, in which he pointed out its eminent significance for colloid chemistry. In 1910 FREUNDLICH [26] made an attempt to explain the discharge on the basis of electrolyte adsorption (see the discussion of Fig. 35 on p. 71) which enabled him to account for the exceptions to the valence rules of SCHULZE, HARDY, WHETHAM, and others.

The numerous investigations on colloid-chemical subjects published in the years 1900–1910 advanced the theoretical speculations to such an extent that comprehensive texts began to appear. As early as 1905, ZSIGMONDY wrote "*Zur Erkenntniss der Kolloide*" (translated by ALEXANDER under the title, "Colloids and the Ultramicroscope," New York, 1909), in which his pioneer researches with the new instrument, mainly on colloidal gold,[27] are described.

Some years later, in 1909, two more comprehensive works appeared, viz.: WO. OSTWALD'S "*Grundriss der Kolloidchemie,*" of which unfortunately no complete second edition exists (only part of it was published in 1911); and HERBERT FREUNDLICH'S "*Kapillarchemie.*" The aim of the latter text is to place colloid chemistry on the basis of capillarity-physics. This book may be considered the standard volume on physico-chemical colloid chemistry (a second edition appeared in 1922; the third edition of 1924 differs from the previous one only by the inclusion of a few additions; an English translation by HATFIELD under the title "Colloid and Capillary Chemistry" was published in 1926).

In 1912 the first edition of ZSIGMONDY'S "*Kolloidchemie*" (English translation by SPEAR, "The Chemistry of Colloids," New York, 1917) was published. This was rather systematic in character, while the later editions have tended more and more in the direction of a general theoretical orientation. The latest German edition in two volumes (Fifth Edition, Leipzig, 1928) is an excellent handbook.

During the present decade, the statics of colloids has made great progress. The investigations of THE SVEDBERG and those of PERRIN, mentioned in detail in Chapter IX, have paved the way for the recognition of a far-reaching morphological similarity between colloidal and true solutions and have emphasized the significance of the idea of degree of dispersion for a clear understanding of various systems.

61. Latest Developments.—In the preceding chapters the most recent research work and the latest theories, were, for obvious reasons, particularly emphasized. The general conclusion is that modern colloid chemistry is developing along the line of the electrical interpretation. Some investigators, including JORDIS [28] and DUCLAUX [29] have, however, devoted more attention to other phenomena, with the hope of making a connection between colloidal and true solutions. But the work of ELISSAFOFF, KRUYT, POWIS and ELLIS, and numerous investigations made in the laboratories of FREUNDLICH, DONNAN, BANCROFT and KRUYT, and quite recently also those performed in the laboratories of British India (among which that of MUKHERJEE stands out prominently) have clearly brought out the great importance of the electric charge. The nature of the electric double layer becomes more and more the central problem of physico-chemical colloid chemistry; and

GOUY's extension of HELMHOLTZ's classical theory gains continually in importance. It seems therefore, at times, as if the adsorption theory so strongly advocated by FREUNDLICH is losing a good deal of its importance. The connection between ionic adsorption and charge is, nevertheless, unmistakable, although we do not yet grasp its real meaning. This fact was pointed out very distinctly by VON SMOLUCHOWSKI in the valuable article which he contributed to GRAETZ's "*Handbuch der Electrizität und Magnetismus*";[30] and the latest discussions (see, for instance, an article by STERN [31]) concede the necessity of introducing an adsorption potential. It cannot be denied that the idea of "ionic adsorption" is used rather flippantly in recent colloid-chemical literature, and it remains for future research to explain satisfactorily the whole mechanism of the genesis and the destruction of the double layer.

A considerable number of comprehensive texts have been published recently. In addition to those mentioned before, attention is called to the following books: W. D. BANCROFT'S "Applied Colloid Chemistry; General Theory," Second Edition, New York, 1926; PAUL BARY'S "*Les Colloides*," Paris, 1921; E. F. BURTON'S "The Physical Properties of Colloidal Solutions," Second Edition, London, 1921; THE SVEDBERG'S "Colloid Chemistry," Second Edition, New York, 1929; and the extensive compilations of R. H. BOGUE, "The Theory and Application of Colloidal Behavior," New York, 1924, and of JEROME ALEXANDER, "Colloid Chemistry, Theoretical and Applied," New York, 1926 and 1928. Two important publications by H. B. WEISER are: "The Hydrous Oxides," New York, 1926, and "The Colloidal Salts," New York, 1928.

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PART III

Emulsoids

CHAPTER XII

GENERAL PROPERTIES OF EMULSOIDS

62. Introduction.—The characteristic differences between suspensoids and emulsoids were discussed on page 10. As stated there, the essential difference evidently lies in the fact that emulsoids exhibit a close relationship between the dispersed particle and the dispersion medium, while suspensoids lack this property. The physical characteristics of suspensoids deviate but little from those of water, while emulsoids form liquids with properties that differ considerably from those of water.

This contrast, however, does not hold for all physical properties; density and light refraction are additive properties for *all* sols; i.e., these quantities change in proportion to the concentration of the colloidal constituent.[1] Regarding the surface tension, the available data are not sufficiently accurate to warrant a conclusion. The statement is often made that emulsoids lower the surface tension appreciably, while the surface tension of suspensoids is practically identical with that of the dispersion medium. Insofar as emulsoids are concerned, this assertion is due to a misconception. It is said, for instance, that gelatin lowers the surface tension of water considerably, whereas, as a matter of fact, the best grades of gelatin, which contain few decomposition products, have no appreciable effect. The depression of the surface tension is frequently caused by impurities in true solution. The effect of soaps on surface tension will be considered in Chapter XVII.

There is one property, however, in which emulsoids differ characteristically from the water which acts as their dispersion medium. This property is viscosity. One would expect, *a priori*, that this quantity would change additively with the amount of dispersed substance, in accordance with EINSTEIN's formula[2] for the relation between the viscosity of a disperse system, η_s, that of the dispersion medium, η_o, and the volume of the dispersed particles, ϕ:

$$\eta_s = \eta_o(1 + \tfrac{5}{2}\phi).$$

It should be noted that this increase in viscosity depends on the *total volume* of the particles, irrespective of the degree of dispersion.

The equation holds, however, only under certain conditions: the particles should be spherical, elastic, and large in comparison with the molecules of the dispersion medium. If these requirements are met, the results obtained agree well with the formula.

Bancelin [3] has tested the equation with a mastic sol and has been able to verify it, except for a small deviation in the value of the constant.

The formula of Einstein may be written in the form:

$$\frac{\eta_s}{\eta_o} - 1 = \tfrac{5}{2}\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the quotient $\frac{\eta_s}{\eta_o}$ expresses the *relative viscosity* of the sol; i.e., the value of the viscosity if the dispersion medium is selected as the standard of reference for which the viscosity is unity. Hence, $\frac{\eta_s}{\eta_o} - 1$, or $\frac{\eta_s - \eta_o}{\eta_o}$ is the increase in the relative viscosity due to the dispersed substance; this quantity is, therefore, proportional to the dispersed volume.

In applying this reasoning to emulsoids, we meet with a peculiar contradiction. For instance, if a polysaccharide like agar-agar is dissolved in water, sols of extremely high viscosity are obtained. A sol containing $\frac{2}{7}$ per cent agar-agar should have a relative viscosity, according to Einstein's formula, of:

$$1 + \tfrac{5}{2} \times \tfrac{2}{7} \times 0.01 = 1.007,$$

if we assume the specific volume of agar-agar to be equal to unity. The experimental value for the relative viscosity is, however, in the neighborhood of 2.400.[4]

Since ϕ is the only variable that determines the phenomenon, the total volume has not been properly accounted for in our calculation. The volume of the dispersed particles is obviously much greater than that of the dry substance used in the computation. Hence, there must be a reason why the particles in the sol are too large in comparison with the volume of the dry agar-agar. It is difficult to explain this fact in any other way than by assuming that the agar-agar particles have taken on a large amount of water, thereby greatly increasing their volume. According to our previous calculation, these particles should have a volume 200 times that of the particles of the dry substance. The quantitative correctness of this figure is subject to certain reservations. In the first place, as we shall see presently, the formula of Einstein needs a certain correction, and, secondly, it is not strictly applicable to systems having a viscosity which differs considerably from that of the dispersion medium. Special investigations have shown that even in dilute sols there is a considerable discrepancy between calculated and observed viscosity; hence, the particles in the agar-agar sol must take up a considerable amount of water.

At first sight, some may be opposed to the idea of ascribing to a sol particle such an unusually great power of absorbing water. It should be realized, however, that a sol containing as little as $\frac{1}{7}$ per cent agar-agar sets into a jelly at room temperature, which means that agar-agar removes the liquidity from an amount of water equal to 700 times its own volume. We are so familiar with these phenomena of gelatinization that we almost take them for granted, and we are not impressed until we meet cases, similar to that just mentioned, where a particle is supposed to imbibe approximately 200 times its own volume.

We do not know in what particular manner the particles take up the water. It is possible either that they swell like sponges or that they surround themselves with a layer of water. Against the latter assumption it may be argued that in this case the particles would exert their action over a distance far in excess of their radius, since the added film of water would undoubtedly be more than one molecule thick. In the following pages we shall, nevertheless, speak of a water layer, because this idea permits, in several respects, the simplest method of representation. (See also Sec. 72.)

63. Viscosity.—As stated in the previous section, the viscosity of sols leads us to believe that they contain strongly *hydrated* particles. In a discussion of this property, the first question that arises is whether, generally speaking, we can consider the viscosity of a sol in the sense of Poiseuille's law.(*Cf.* reference 22, p. 189.)

A great deal of controversy has centered around this problem. In the first place, there is no agreement as to how the viscosity of a sol really should be measured. We can, of course, use the well-known Ostwald viscometer (Fig. 84), which is quite satisfactory for relative measurements, provided its construction is such that certain systematic errors are eliminated.[5] Some investigators seem to think that this is not possible, and for that reason use viscometers which operate on other principles. Among these are the viscometer of COUETTE,[6] which measures the friction of a cylinder rotating in a liquid, and the viscometer of HESS,[7] in which the liquid under investigation and a standard liquid are separately forced through a capillary tube by means of air pressure.

Whatever instruments have been used, the conclusion reached by various investigators is that emulsoids, as a rule, do not follow the law of POISEUILLE; i.e., different viscosities are found, depending on the rate of capillary flow. This behavior is explained by saying that the sols not only have a liquid viscosity but possess also a certain elasticity such as we find in solids.

It seems to the author that these objections are, for the greater part, unfounded.[5] If we investigate sols in properly constructed viscometers, carefully accounting for the changes which the sol undergoes as a result of irreversible and hysteresis phenomena, and, furthermore, if we take care to exclude sols that gelatinize, the results obtained are in complete accord with the law of POISEUILLE. Moreover, there is a complete absence of elastic phenomena. Only when we are dealing with particles that deviate sharply from the spherical shape, as for instance, those of the V_2O_5 sol (*cf.* p. 143), benzopurpurin, and possibly partially gelatinized sols, do the results fail to conform to the formula of POISEUILLE.

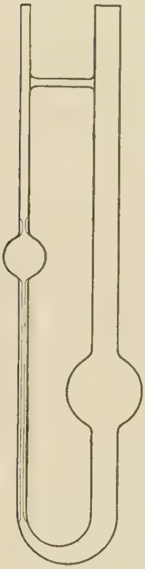

FIG. 84.

In applying EINSTEIN's expression to sols of different concentration, one might expect to find a simple linear relation between the relative viscosity and the concentration of the sol. Investigations on different sols confirm the formula approximately. The small deviation from the rectilinear behavior might be explained by assuming that the hydration of the particles is a function of the concentration. In the next section (64) we shall meet with a second phenomenon, the electro-viscous effect, which may be a function of the concentration and hence may cause the discrepancy. Apart from these small deviations in the values for the relative viscosity, appearing in the third decimal only, it may be said that Einstein's formula reproduces the observations with sufficient accuracy for sols of agar-agar,[8] gum arabic,[9] starch,[11] etc.

64. Electro-viscous Effect.—When the viscosity of a sol is studied in relation to the concentration of an added electrolyte, for instance, that of barium chloride,[10] the results obtained lead, for a sol of agar-agar, to the following graphical representation (Fig. 85). On the addition of the first milli-equivalents a decided drop in the viscosity is observed, while on further addition of the electrolyte the viscosity remains practically unchanged. The pronounced effect of very small amounts is strikingly reminiscent of the behavior of capillary electrical processes previously discussed (Chapter III). The agar-agar sol is negatively charged; hence, we are dealing, presumably, with the effect of an ion of opposite charge, i.e., the Ba ion. By carrying out similar experi-

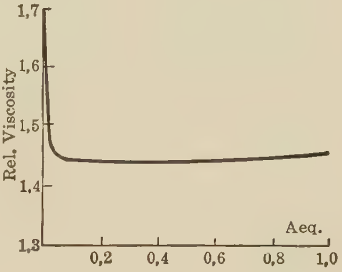

Fig. 85.

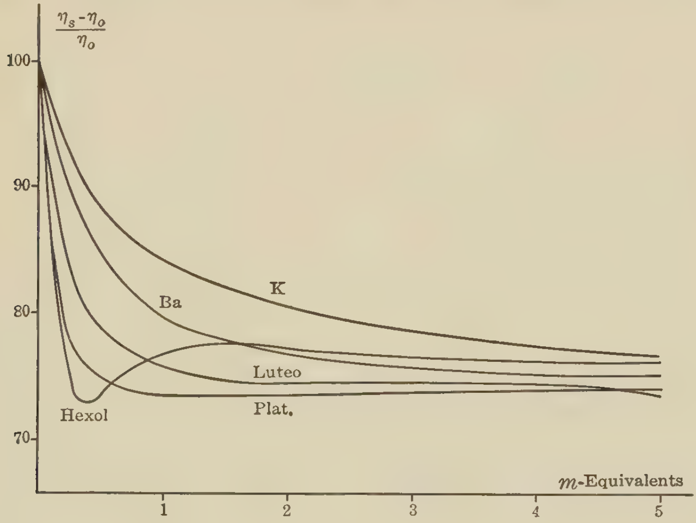

Fig. 86.

ments with electrolytes having cations of a different valence, we actually find that the lowering of the relative viscosity is greater the higher the valence of the cation. Fig. 86 shows the changes in viscosity for a starch sol on the addition of various ions. The salts used are indicated for each type of curve.[11] By luteo is meant the luteo cobalt chloride with its trivalent cation. The curve marked Hexol will be referred to later.

In Fig. 87 the same phenomenon is illustrated for the agar-agar sol. Here too,[10] the effect of the valence of the cation is quite noticeable, while that of the anion is very small. The experimentally determined curves for the monovalent cations fall within the upper black band; those for the divalent cations, within the second band; and so on.

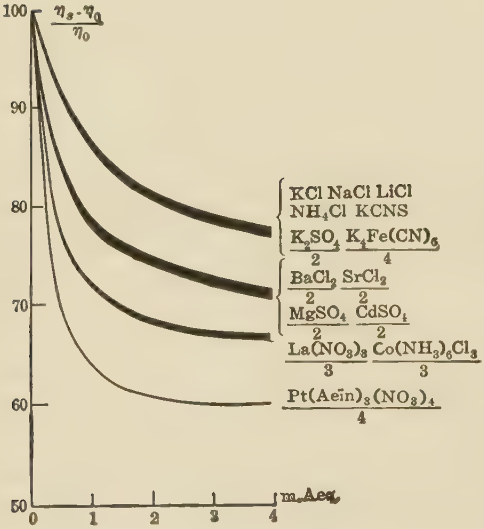

FIG. 87.

The similarity of these results to those obtained in capillary electrical phenomena immediately suggests the possibility of a relation between the electrical charge of the particles and its effect on the viscosity of a sol. In 1916, VON SMOLUCHOWSKI showed that the expression of EINSTEIN holds in reality only for uncharged particles.[12] In case the particles are electrically charged, they are surrounded by a repelling sphere (*cf.* p. 117) whereby their active volume is virtually increased. This apparent increase in the active volume might be called the "quasi-voluminous" effect. Henceforth, we shall speak of the *electro-viscous effect,* by which we mean the increase in relative viscosity as a result of the electric charge of the particles. A relation between viscosity and electric charge had previously been mentioned by HARDY and by WO. OSTWALD.[13]

Von Smoluchowski deduced the following modification of Einstein's expression:

$$\frac{\eta_s - \eta_o}{\eta_o} = \frac{5}{2}\phi\left[1 + \frac{1}{\kappa\eta_o r^2}\left(\frac{\zeta D}{2\pi}\right)^2\right], \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where κ is the specific conductance, r the radius of the particle, D the dielectric constant, and ζ the electro-kinetic potential of the electric double layer, referred to previously.

In complete accord with the results just mentioned, it has been found in experiments on the sol of starch that polyvalent ions can actually reduce the charge to zero or else reverse it.

In Fig. 86 the curve marked Hexol indicates the change in the viscosity of the sol caused by additions of a hexol salt

$$\left[\mathrm{Co}\left\{(\mathrm{OH})_2\mathrm{Co}\; en_2\right\}_3\right](\mathrm{NO}_3)_6$$

where en_2 represents ethylene diamine. It will be seen that this hexavalent cation produces, first, a lowering and then, by a reversal of the charge, a rise in the viscosity (*cf.* p. 90). The boundary potential ζ appears squared in equation (2); hence its sign is without effect on the electro-viscous effect.

65. Cataphoretic Phenomena.—The fact that we can investigate electrical phenomena by means of viscosity experiments simplifies the study of emulsoids considerably. Direct observation of cataphoresis in emulsoids is made difficult by the fact that these sols are colorless. The use of Burton's apparatus (*cf.* p. 60) is therefore excluded. A makeshift arrangement would be to observe at right angles the path of a ray of light passing through the cataphoretic tube. The supernatant water gives no Tyndall effect, while the emulsoid sol does. Thus, the migration of the boundary under the influence of the electric current becomes visible.[9] Svedberg [14] used another expedient, that of illuminating the apparatus with ultraviolet light and studying the fluorescence of the emulsoid sol photographically. In dealing with proteins, one may follow the movement of the albumin by allowing the cataphoresis to take place in separate vessels or else in an apparatus with different compartments separated by stopcocks (Fig. 88). Albumin migrates from C into A or B, which were filled originally with water. From a Kjeldahl determination of the contents of A or B we can get an idea of the amount of emulsoid transported by the current.

In applying this last-named method to the calculation of the potential of the double layer, from the measurements of the amount transported, we meet, however, with a serious difficulty. On page 84 appeared the formula:

$$\zeta = \frac{6\pi\eta}{HD} \cdot u, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

whereby it was assumed that the potential gradient throughout the cataphoretic space changes gradually. This condition is not fulfilled, however, when constrictions due to stopcocks or siphons occur, and the resulting error affects the computation.

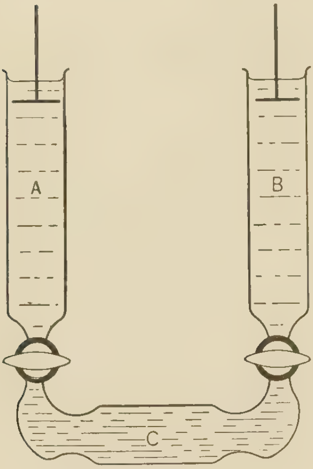

FIG. 88.

Unlike suspensoids, proteins have an electric sign which depends strongly on the medium. A suspensoid sol has an electric sign which is positive or negative according to the nature of the material forming the particle. Only for substances like tin oxide does the charge depend on the peptizer. In general, however, only strongly capillary-active ions, such as polyvalent ions and those that are strongly adsorbed, can bring about a reversal of charge (see p. 90).

For albuminous sols, however, matters are entirely different. These sols are either positive or negative, according to the hydrogen ion concentration of the medium. Very slight changes in the hydrogen-ion concentration may produce a complete reversal of the electric sign. (For further particulars, see Chapter XIV.)

The measurement of the electro-viscous effect has been compared in many cases with direct measurements of cataphoresis, and has led to satisfactory, at least semi-quantitative agreement.[8, 9, 10] Consequently, we shall, henceforth, often draw conclusions regarding the electric charge of the particles from the results of experiments dealing with electro-viscous effect. Furthermore, a comparison of electro-viscous effect and cataphoretic velocity has produced results which permit an estimate of the size of emulsoid particles.

66. Size of Emulsoid Particles.—It is possible to draw conclusions regarding the size of emulsoid particles from determinations of electro-viscous effect and cataphoresis.[15] For instance, if the viscosity of a sol is determined at two concentrations of an added electrolyte, each of the two values obtained must satisfy the above-mentioned equation (2). By determining the cataphoretic velocity, u, of the sol at the same electrolyte concentrations, we can calculate the boundary potential from these measurements each time by means of formula (3).

Substituting these values of ζ in the first two equations (2), we get two expressions in which all quantities are known except ϕ and r. By eliminating ϕ, the value of r can be computed. Experiments on the sol of starch have indicated that the diameter of the particles is in the neighborhood of 14 mμ. Tendeloo[16] has shown that this method likewise gives good results in the determination of the size of suspensoids.

In this manner we can obtain the size of the particles, including the surrounding film of water. It is possible, however, to find out from the viscosity determinations which part of the active volume must be ascribed to the dry substance, the remainder being due to the water film. From this we can compute the part of the emulsoid, which is taken up by the dry substance, the difference between unity and this value being accounted for by the water. In the case of starch, the amount of dry substance corresponds to a particle having a diameter of 6 mμ.

In the above calculation it was assumed, however, that ζ varies on the addition of an electrolyte, but that ϕ and r do not. Unfortunately, we cannot, *a priori*, predict that this will be so. The result depends on the relation which exists between hydration and electric potential at the boundary of the particle. From the fact that varying concentrations of electrolyte give the same results for r, it seems that for substances like agar-agar and starch such a connection does not exist; for gum arabic and proteins, on the other hand, it exists.

These investigations indicate that the size of the particles of an emulsoid sol, such as starch, is of the normal order of magnitude of colloidal particles. This size far exceeds molecular dimensions; hence, it is highly improbable that we are dealing with a simple dispersion of large molecules. Röntgenographic investigations have developed a suitable method for arriving at the size of the corresponding *molecules*.

On page 134 reference was made to the method of DEBYE and SCHERRER for the determination of the crystal properties of suspensoid particles. Emulsoid particles do not give, generally speaking, X-ray patterns with well-defined interference rings. Various threads occurring in nature give, however, distinct photograms. Ramie and cotton threads in particular have been studied by HERZOG and JANKE.[17] These fibers appear to consist of oriented particles with unmistakable crystal properties. From the X-ray pattern, the space lattice of the crystals and the size of the elementary cube can be determined. Assuming that in such an elementary cube only one molecule occurs (probably there are more, so that the molecular size is only a fraction of the figure mentioned here), we find by computation that the molecule of cellulose has a volume not exceeding 0.68 $m\mu^3$. The starch molecule is surely not larger than that of cellulose; consequently, we arrive at the conclusion that a particle in the emulsoid sol consists of several thousand molecules.

In recent times, chemical arguments have been advanced which seem to indicate that the cellulose molecule is not exceedingly large.[18] It has been erroneously assumed in organic chemistry that n, in the formula $(C_6H_{10}O_5)_n$, is large; in reality, this quantity is completely unknown since we lack the means of determining the molecular size of a non-volatile and insoluble (i.e., non-molecularly dispersible) substance. From the researches of BERGMANN[19] and those of PRINGSHEIM,[20] one gains the impression that there is a possibility of obtaining cellulose temporarily—although only under unstable conditions—as a monomolecularly dispersed substance, in which case $n = 1$ according to the ebullioscopic method. These chemical investigations are thus a confirmation of the concept developed here, viz., that sols are polymolecularly dispersed particles. Other experiments of BERGMANN[21] prove that the development of the organic chemistry of proteins is proceeding in the same direction.

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CHAPTER XIII

STABILITY OF EMULSOIDS

67. General Characteristics.—Whereas the proteins have long been known to be the most typical emulsoids, nevertheless, these sols are discussed in numerous articles and texts as if they were solutions of electrolytes with large molecular weight.[1] In the previous section we saw that the particle size of emulsoids is incomparably greater than that of the largest known molecules and that, on the other hand, there is no reason to assume that the molecules of various substances entering into emulsoid solution are particularly large. It is obvious that a colloidal particle can be built up from small molecules: a gold sol consists of gold particles formed from atomic gold; the As_2S_3 molecule is small, although the arsenic trisulphide exists in the state of colloidal subdivision in water.

There is, however, a special reason which has led many investigators to look upon emulsoids as molecularly dispersed systems, more particularly, as electrolyte solutions; this is the fact that a great many properties of protein solutions may be explained by considering these solutions as systems of *amphoteric electrolytes*. This train of thought will be fully considered in the next chapter and shown to be incorrect. It may be pointed out at this place that a discussion of emulsoids in terms of ionically dispersed systems must necessarily conflict with typically colloidal properties of these systems. We do not know any electrolyte solutions that scatter the light in a corresponding manner (TYNDALL effect), show no lowering of the freezing point or rise of the boiling point, and produce, for such minute concentrations, such exceedingly viscous solutions. The fact that protein solutions do not pass through dialysis membranes might possibly be explained on the basis of a large number of atoms in the molecule (*cf.* p. 159), but the other properties mentioned here cannot be connected with large chemical molecular weight without leaving the domain of general chemical experience.

The main criticism that can be raised against the concept of the electrolyte nature of protein solutions lies in the fact that the division of colloids into suspensoids and emulsoids would thus be without continuity. In other words, we should have to ascribe to colloid chemistry a dualistic line of reasoning which is highly unsatisfactory. Whereas, for instance, the electrical properties of suspensoids are to be explained by means of the electro-adsorptive phenomena of the peptizing ions which divide themselves between the particles and the medium in accordance with the adsorption isotherm, we should have to consider for protein solutions an ionic equilibrium of one single kind of molecules dissociated into ions, the degree of dissociation being governed by OSTWALD'S dilution law.

This dualistic theory of colloid chemistry has found considerable support, as stated before, in the specific properties of protein solutions. For a clear understanding of the condition of emulsoids, it will be wise not to start with the study of proteins, which always opens up the possibility of an electrolytic point of view, but to investigate the corresponding properties of higher carbohydrates, thereby precluding an electrolytic explanation.

In the previous chapter we saw that researches on the electro-viscous effect have brought out clearly that typical emulsoid sols, such as those of agar-agar and starch, possess an electric charge which is in no way different from that of suspensoids. Hence it is irrational to place the electro-chemistry of emulsoids on any other basis than that of suspensoids. Although some investigators have made an attempt to transform the electro-chemistry of suspensoids by considering, for instance, an Fe_2O_3 particle as a complex ion, it may be said that this idea is unsound and leads to unsatisfactory conclusions. One unavoidable inference of that train of thought is obvious: that flocculation of colloids (including suspensoids!) must be considered as a transgression of the solubility product. This line of reasoning, however, destroys all continuity between capillary electrical phenomena and flocculation, whereas, as a matter of fact, the close relation between these two properties has led to a satisfactory explanation of the flocculation of suspensoids (*cf.* Chapters IV and V). In fact, nobody has ever faced the consequences of bringing these phenomena within the domain of the theory of the solubility product.

Our experiences concerning the electro-viscous effect compel us to discuss emulsoids on a par with suspensoids. As we shall see in the next section, this can be done without any difficulty.

68. The Two Stability Factors.—An important difference between suspensoids and emulsoids lies, as we have seen, in the fact that the latter, when deprived of their electric charge, do not flocculate. This is exactly the point which has led to a separation of the statics of emulsoids from that of suspensoids.

In order to explain this difference, we must look elsewhere for a suitable hypothesis which can be tested experimentally. Evidently, emulsoids have *a second stability factor* which prevents the flocculation of the uncharged particles. Remembering that the condition of non-flocculation signifies a probability of adhesion not largely deviating from zero (p. 117), we realize that this second factor, which keeps the colliding particles from permanently uniting, must be of a different nature. Since, as shown on page 181, the characteristic difference between suspensoids and emulsoids is due to the hydration of the particles, we immediately assume that it is the film of water which furnishes a second protective factor. In other words, emulsoid particles may be protected against flocculation both by their electric charge and by their hydration. When we have at our disposal a means of eliminating hydration, we can readily verify this assumption. On the other hand, we shall see, in a later section (Sec. 72, p. 201) why hydration can prevent the union of colliding particles.

Alcohol is well known to be a strong dehydrating agent, presumably on account of the formation of hydrates in solution up to a considerable concentration. The pronounced maximum in the viscosity curve for solutions of alcohol and water clearly points in this direction.[2] This hydration of alcohol, therefore, is a phenomenon which is governed by the law of mass action, since the latter determines the equilibrium between the alcohol hydrate(s) and the decomposition products.

On adding alcohol to an emulsoid sol, for instance, that of agar-agar,[3] we find that the addition of a few per cent has little effect. However, on approaching the concentration at which hydration predominates, i.e., where water is strongly bound by alcohol and thus removed from the particles of agar-agar, we notice a very remarkable phenomenon. The sol changes its properties very strikingly in two directions: viz., the viscosity decreases quite rapidly, and the optical properties become those of a suspensoid. In other words, the sol acquires the bluish tinge (Tyndall light) of a mastic sol. In the ultramicroscope the indistinct Tyndall cone of the original sol changes to a well differentiated picture, such as the one we know for suspensoids. In short, the emulsoid sol has been transformed by the alcohol into a suspensoid sol as a result of the dehydration of the agar-agar particles. Such phenomena as these have already been mentioned in 1913–14 by Scarpa.[4]

This fact, remarkable in itself, is supplemented by another which completes the argument. By dehydrating the sol we have removed the second stability factor but left the first: viz., the electric charge, intact. The small amount of electrolyte required for the removal of the capillary electric effect will be sufficient to flocculate the sol. As a matter of fact, the agar-agar sol dehydrated by alcohol is just as sensitive to electrolytes as any of the suspensoid sols discussed in Part II of this book.

In the following table are reproduced some of the flocculaton values obtained with such a dehydrated sol. The characteristic discharging properties, in connection with the valence of the oppositely charged ion, will be immediately recognized.

TABLE XXIV

One Volume of Agar-agar Sol+5 Volumes of Alcohol

Electrolyte	Flocculation value in millimoles per liter
KCl	1.25
$BaCl_2$	0.05
$[Co(NH_3)_6]Cl_3$	0.03

We have already seen that the addition of minute quantities of an electrolyte to a starch or an agar-agar sol removes the charge but not the stability. On adding alcohol to such a discharged sol, one observes an immediate flocculation. This proves, therefore, that we are dealing, in every case, with two stability factors but that it is immaterial in which order they are removed. The removal of one can be accomplished without evident effect, but the removal of both inevitably causes flocculation.

It was stated on page 68 that the flocculation of suspensoids does not require a *complete* removal of the charge. A lowering of the potential to its critical value is sufficient to cause precipitation. A similar statement can be made with regard to hydration. Since these two factors both determine the probability of adhesion, and since, for flocculation, the probability of adhesion must be raised to a definite value in the neighborhood of unity, they can be lowered simultaneously and thus bring about flocculation. In other words, in the same sense that we speak of a *critical potential* (in the absence of hydration) we might consider a *critical hydration* (in the absence of charge). Between these two values will be found a series of conditions for which flocculation becomes possible by a simultaneous lowering of charge and hydration, both to values above their critical limiting values.

This explains why we find widely differing "alcohol numbers" for variously charged emulsoids. The alcohol number may be defined as the number of cubic centimeters of alcohol which must be added to 5 cc. of sol in order to secure flocculation. This number is obviously the larger the higher the charge of the sol. This point will be referred to later (see p. 212).

A suitable plan for forming an idea of the dehydration of the particles by means of alcohol is to study the relative viscosity of the sol on the addition of increasing quantities of alcohol. A decrease in the relative viscosity means a lowering of ϕ, and hence a shrinkage of the film of water surrounding the particles. Special emphasis should be placed on the expression *relative* viscosity, since the viscosity of water alone is considerably changed by alcohol. Figure 89, therefore, gives the change for both systems: water + alcohol and agar-agar sol + alcohol. By dividing the corresponding viscosities we obtain the changes in *relative* viscosity, viz., $\frac{\eta_{\text{sol}}}{\eta_{\text{disperse medium}}}$ as represented by the curve shown in Fig. 90. We notice that the dehydration becomes very marked for a weight concentration of about 45 per cent alcohol.[5]

Acetone is likewise a suitable dehydrating agent and gives similar results. Other dehydrating substances, such as sulphuric acid or glacial acetic acid, may be employed; but since these compounds are electrolytes, they affect both hydration and charge. The effect of this combined action will be discussed in Sec. 69.

69. Salting Out.—We have previously (p. 10) seen that emulsoids can be precipitated by means of electrolytes but that much greater quantities are required than in the case of suspensoids. This phenomenon is called "salting out," an expression which indicates that the reaction taking place is quite different from flocculation.

There are certain salts which are, in general, suitable for salting out emulsoids, viz., $(NH_4)_2SO_4$, $MgSO_4$, and Na_2SO_4. These salts are very soluble; hence, they can be used in comparatively large concentrations without being disturbed by the limit of solubility. However, the solubility of a salt is not the only factor which determines whether it is suitable for the purpose of salting out. $MgSO_4$ is less soluble than $MgCl_2$, and yet it can be employed to salt out agar-agar whereas the chloride is unsuitable even at the highest concentrations.

It has been shown that the power of salting out depends on both the nature of the cation and that of the anion. The different cations can be arranged in a series of decreasing precipitating power, from left to right, when used in equal molecular concentration. A similar series exists for anions. These series are called *lyotropic* series.

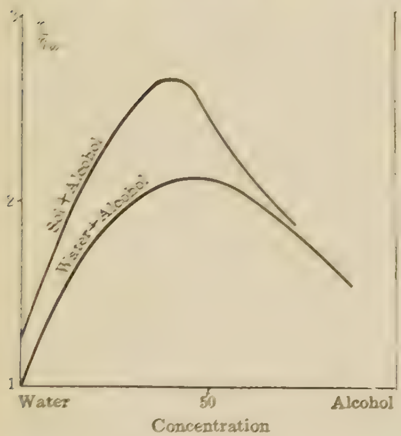


Fig. 89.

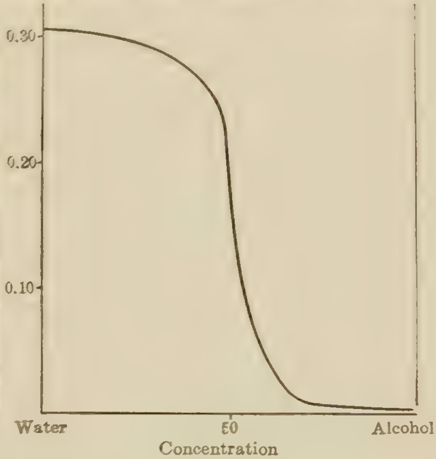


Fig. 90.

Cation series:

Li—Na—K—Rb—Cs and: Mg—Ca—Sr—Ba.

Anion series:

SO_4—Cl—Br—NO_3—I—CNS

These lyotropic series are not only met when emulsoids are salted out but are also characteristic of a number of other physicochemical phenomena. The effect of neutral salts on the *rate of inversion of cane sugar* and on other reaction velocities is determined by the order of the lyotropic ionic series. The same sequence is noticed in the displacement of the *maximum density of water* (at 4°); in the change in *solubility of non-electrolytes*, for instance, that of urea in water; and in the influence on the *surface tension of water*.[6] In the subsequent chapters we shall consider still other properties that are related to these lyotropic series.

The significance of the lyotropic order of ions is best understood from its connection with another phenomenon in which the series also comes to the fore, viz., *the hydration of ions*. From investigations concerning the mobility of different ions,[7] the conclusion has been reached that these ions, generally speaking, carry water molecules along with them. It appears that the degree to which ions are hydrated is determined by the lyotropic series; hence, it is obvious that this series must be regarded as an indication of the order in which the respective ions are hydrated. This hydration, of course, is a reaction which is subject to the law of mass action. The fact just mentioned readily explains the effect of salts on the solubility of other substances: the more water the ions require for themselves, the less remains available as a solvent for the added substance. This practically corresponds to a removal of the solvent. The effect on the reaction velocity (increase of active mass) is likewise easily understood; but the change in surface tension and the displacement of the maximum density (of water) cannot be explained by ionic hydration. It is now generally conceded that the latter is closely connected with the association of the water molecules to di- or polyhydrols: $n\mathrm{H_2O} \rightleftharpoons (\mathrm{H_2O})_n$. The influence exerted by the ions in the order of the lyotropic series is apparently such that those at one end favor association while those at the other extreme promote dissociation. Since surface tension is intimately related to the molecular size of the liquid, it is evident that the same relationship holds for the change of the surface tension in the order indicated by the lyotropic series.

We thus arrive at the inference that a lyotropic series expresses the order in which the ions take up water or affect the association and dissociation of water.

Salting out has, quite naturally, been related to the power of the ions to take up water, a property which formerly caused the impression that the effect of electrolytes on emulsoids merely consisted in withdrawing water from the sol, whereas the influence exerted by electrolytes on suspensoids was considered to be due to capillary electrical phenomena. In the light of the experiments sketched in the preceding sections, however, the effect on emulsoids appears to be less one-sided. We now realize that the small initial amount of added electrolyte fully performs its capillary electrical task and that the removal of water is brought about subsequently in the order of the lyotropic series. This argument can be readily verified by studying the change in relative viscosity as a function of the salt concentration.

Figure 91 shows how the relative viscosity of an agar-agar sol varies when $MgCl_2$ or $MgSO_4$ is added. The curve as drawn shows that the first few millimoles added eliminate the electroviscous effect. The valence of the Mg ion is the determining quantity; hence, both curves coincide. At higher concentrations the effect of the dehydration is felt, and this effect is greater for the sulphate than for the chloride in accordance with the position of these two ions in the lyotropic series. We notice that the curve for the sulphate lies lower and soon descends rapidly, thus resembling closely the alcohol-dehydration curve represented in Fig. 90, the difference being that in the latter case the dehydration is *not* preceded by a removal of the charge, so that the dehydrated emulsoid remains stable. The magnesium sulphate, however, dehydrates a discharged emulsoid and consequently causes a simultaneous flocculation. The sulphate curve, for this reason, cannot be continued very far on the descending lower part as the viscometer soon becomes filled with flakes.

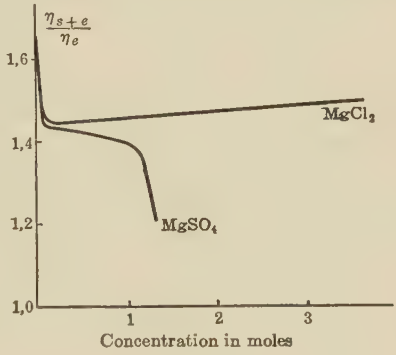


Fig. 91.

The theory presented here indicates, therefore, that salting out consists in a discharge followed by dehydration. In other words, it is equivalent to a removal of *both* stability factors, which brings this phenomenon in line with the viewpoints developed in this chapter.

The action of sulphuric acid and glacial acetic acid, mentioned at the end of Sec. 68, need not be discussed separately since these substances act in a similar manner. Another side of the problem of lyotropy will be further discussed on page 257.

70. Dehydration by Tannins.—It is a familiar fact that tannin solutions precipitate various emulsoid sols. For example, the mutual precipitation of tannin and gelatin is a well-known qualitative reaction, and the transfer of emulsoid material (particularly proteins) into insoluble forms of matter by means of tannin has long been the basis of the theory of tanning.

Other sols, like those of agar-agar and starch, can likewise be precipitated by tannin.[8] Careful investigation has shown that the addition of tannin to emulsoid sols free from electrolytes does not necessarily produce flocculation; but if, on the other hand, tannin is added to a sol such as that of agar-agar, the latter is changed from the emulsoid into the suspensoid condition. The sol containing tannin has a milky appearance (TYNDALL light), shows a well-differentiated ultramicroscopic picture, and possesses a viscosity which differs only slightly from that of water. The sol becomes very sensitive to electrolytes, and the effect due to the electrolytes present depends entirely on the valence of the ion of opposite charge. In short, we are dealing with a sol which has purely suspensoid properties; the agar-agar sol treated with tannin shows great similarity to the sol dehydrated by alcohol. On account of the decreased viscosity, we are safe in stating that tannin has dehydrating properties and acts in a way similar to alcohol.

The disappearance of emulsoid properties is also indicated by the fact that an agar-agar sol treated with tannin no longer gelatinizes on cooling, a property characteristic of hydrated particles (*cf.* p. 229).

There is, however, one striking difference between the dehydrating action of alcohol and that of tannin. Minute quantities of the latter are sufficient to bring about dehydration, whereas the action of alcohol becomes noticeable only in weight percentages in excess of 50 per cent. Since the same effect is produced with 1 per cent of tannin, the mechanism of dehydration by tannin must be entirely different from that caused by alcohol. It is reasonable to explain the difference as follows:

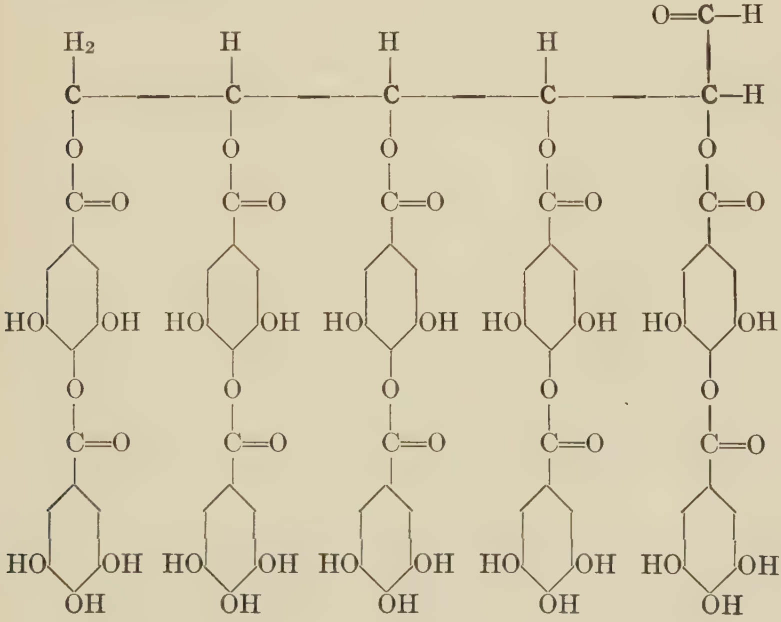
We saw previously that the dehydration effected by alcohol results from the mass-law equilibrium between alcohol and water (see p. 192). Tannin, on the other hand, is a substance which lowers the surface tension considerably; in other words, it is strongly adsorbed. Hence, the large effect in small concentrations is presumably due to the adsorption of tannin by the colloidal particles.

That this is really the case can be proved in the following manner: When another compound that is capable of exerting a displacing action (*cf.* p. 40) is added to an agar-agar sol treated with tannin, the colloidal particles are freed, at least partly, from the adsorbed tannin; and, consequently, the emulsoid properties must return. Curiously enough, we can use, for instance, alcohol for this purpose. Investigation has shown that alcohol added in small amounts to an agar-agar sol, that has been dehydrated by tannin, increases the relative viscosity and brings back the property of gelatinizing, whereas the addition in quantities of about 50 per cent again prevents the setting of the sol as a result of the dehydration by alcohol.

This shows that the action of tannin on emulsoids agrees with our ideas concerning the stability of emulsoid sols. Tannin is a dehydrating agent, but the principle on which it acts is different from that which governs the action of alcohol. In interpreting this dehydrating action, we might point out the following: Tannin is penta-digalloyl-glucose:

$$C_6H_7O_6[COC_6H_2(OH)_2OCOC_6H_2(OH)_3]_5,$$

and has the structure:



When this substance is adsorbed, it will probably turn the glucose end of the chain toward the particle and the phenol groups toward the water, according to the theory of LANGMUIR and HARKINS (see p. 41). The outside of the particle will no longer be covered by its own hydrophile molecules but by phenol groups. Since the simplest phenol is only partially miscible with water, and since, moreover, the miscibility for complicated phenols decreases, it is obvious that the hydrophile character of the agar-agar particles will be greatly diminished by the modification of their boundary layer. In an alkaline medium, however, the phenol groups are changed into groups —ONa which are ionized and remain to a large extent hydrophile. Hence tannin does not dehydrate in an alkaline medium.

This remarkable property of tannin is noticed for all depsides to a greater or lesser extent. We find, therefore, that the investigations of BUNGENBERG DE JONG[8] have developed a new method of dehydration, viz., by adsorption of substances having certain definite molecular configurations. The important modifications thus introduced in the system, particularly with regard to the sensitiveness towards electrolytes, may offer a basis for the explanation of various precipitation reactions in nature.

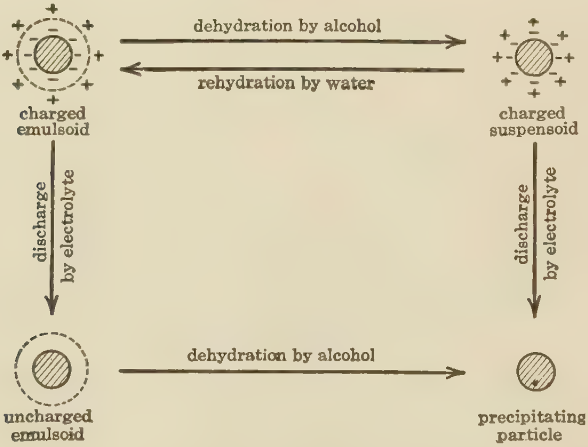

dehydration by alcohol
rehydration by water
charged emulsoid
charged suspensoid
discharge by electrolyte
discharge by electrolyte
dehydration by alcohol
uncharged emulsoid
precipitating particle

FIG. 92.

71. Summary.—Our concept of the stability of an emulsoid sol of the simplest type, such as one of agar-agar or starch, may be embodied in the following sketch (Fig. 92) which will be readily understood. The dehydration of the electrically charged particle is represented as reversible, whereas the removal of the electric charge is not reversible (at least not in a simple way). Furthermore, the dehydration of the uncharged emulsoid is an irreversible flocculation, for, as we have seen, this flocculation is very similar to that of suspensoids; i.e., once the primary particles have united to form flakes of secondary or more complex particles, these flakes cannot by a simple process be broken up into primary particles.

72. Coacervation.—The flocculation of emulsoids is in reality not so simple as it has been represented in the preceding pages. It has been known for a long time that salting out produces the separation of a liquid aggregate instead of a solid one.[9] In such an instance, there are not always formed two distinct layers but a number of various-sized viscous drops. It appears that this separation of a liquid in some form or other is not a specific property of only a few systems but rather a general possibility in all cases where we usually observe flocculation. In fact, the separation of a liquid aggregate is of general occurrence whenever the conditions for the experiment are carefully chosen. Both phenomena, viz., formation of a liquid phase and ordinary flocculation, require a certain degree of discharge and dehydration. The droplets formed, obviously still contain the primary particles since rehydrating influences restore the sol condition. The sol particles have merely been piled or accumulated in the separating drops, a process that is suitably expressed by the term coacervation (acervus, in Latin, means pile).[10]

For a clear understanding of this first stage in the flocculation it is necessary to present a well-defined outline of the phenomenon of hydration and its significance for the stability of emulsoids.

In Chap. I, Sec. 4, the question was raised: Why is it that colloidal particles which possess free surface energy, do not unite? In the case of suspensoids we know that electrical forces prevent material collisions but there is no reason to expect that hydration acts similarly. It is more likely to suspect that hydration influences the free surface energy itself. Now the boundary tension between water and water is zero; hence, the more water the particle takes up, particularly in its periphery, the more it resembles the medium, in other words, the smaller the boundary tension and the probability of cohesion.[11]

Regarding the mechanism of hydration, a few remarks were made in Sec. 62, page 181. It consists, presumably, partly in a localized, spongelike swelling of the particle and for the rest in the acquisition of a surrounding water film. The latter is the seat of the boundary tension which tends to unite the particles. Researches on lyotropy (which will be more fully discussed later; see p. 257) favor the assumption that hydration is mainly an orientation of dipolar water molecules, in such a way that the first layer, the so-called *concrete* layer, is firmly attached to the colloid particle while the succeeding layers of water molecules are bound and oriented to a lesser extent as the orienting forces become weaker and the heat motion more effective. Let us designate the whole of these layers in which there is a gradual transition from oriented to unoriented water by the name of *diffuse* water layer. For particles having both a concrete *and* a diffuse water mantel the drop in free surface energy is small and the probability of cohesion almost negligible. These particles, therefore, are stabilized.

On dehydrating the particles gradually, we remove, obviously, first the diffuse water film. The sol is then no longer stable (at least if no protecting electric charge is present) since there is formed an interface between oriented and unoriented water in which there is, naturally, a considerable drop in free energy. The particles surrounded only by a concrete water film, exhibit a tendency to unite and the resulting coacervated lumps form the drops or the liquid layer mentioned at the beginning of this section. On continued dehydration the drops readily change into solid flakes. Rehydration, for instance the addition of alcohol to a sol previously dehydrated by tannin (see p. 199) or else, the addition of ions such as I′ or CNS′ which favor hydration, restores the sol.

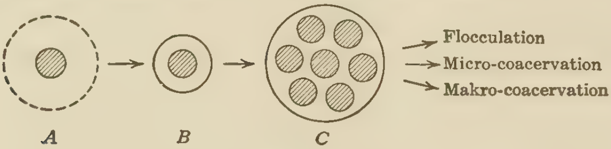


Fig. 92 *bis*.

The mechanism of the process is reproduced schematically in Fig. 92 *bis* where *A* represents a particle surrounded by its diffuse water mantel (dotted periphery) and *B* the same particle with its concrete water film. Coincidently with beginning dehydration (or in general: desolvation) the diffuse mantel shrinks until it finally assumes the dimensions of the concrete film indicated by the solid periphery in *B*. Whenever there is sufficient free surface energy in the film boundaries a number of particles combine to form a coacervate such as the one represented in *C*. Depending on the time during which the process of agglomeration has been going on, we get typical flocculation, micro- or macro-coacervation, viz., there are formed either solid flakes, or drops that coalesce into layers (macro-coacervation) or else small drops visible only under the microscope (micro-coacervation). It is readily seen that the picture of the hydration mantel presented in this section strongly resembles that of GOUY's electric double layer. This is not surprizing in view of the fact that both problems are closely related: In speaking of the double layer we are dealing with ions (in the outer coating) which are to some extent kept in position by oppositely charged ions close to the wall while, on the other hand, hydration deals with water molecules which are oriented (presumably) by chemical forces.

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2. See A. E. Dunstan, Z. physik. Chem. **49**, 590 (1904).

3. H. R. Kruyt and H. G. Bungenberg de Jong, Z. physik. Chem. **100,** 250 (1922); Koll. Beih. **28**, 1 (1928).

4. O. Scarpa and d'Aquino, Rend. Soc. Chim. Ital. II, **5**, 370 (1913); O. Scarpa, Koll. Z. **15**, 8 (1914).

5. The small depression which occurs for smaller percentages of alcohol must be ascribed to the change in electro-viscous effect. It might at the outset appear strange that this electro-viscous effect is altered by a non-electrolyte, but one should remember that in formula (3) on p. 186 there is present the dielectric constant, *D*, which has quite another value for alcohol than for water. This quantity, *D*, is considerably changed by alcohol. This change in ζ is a sufficient explanation for the slight additional depression. The same thing was found by LIER (H. R. Kruyt and H. Lier, Koll. Beih. **28**, 407 (1929) for casein and by TENDELOO (H. R. Kruyt and H. J. C. Tendeloo, Koll. Beih. **29,** 396 (1929) for gum arabic.

6. See Conmar Robinson, Diss. Utrecht, 1929.

7. See E. W. Washburn, Jahrb. Radioact. Electronik. **1908**, 493; **1909**, 69. Also: E. W. Washburn and E. B. Millard, J. Am. Chem. Soc. **37**, 694 (1915).

8. H. G. Bungenberg de Jong, Rec. Trav. Chim. **42**, 437 (1923); **43**, **35** (1924); **46**, 727 (1927); **48**, 494 (1929). The last-mentioned article shows that the explanation, as presented here, needs amplification, insofar as there appears to occur a separation in the boundary layer.

9. See Wo. Ostwald, Koll. Z. **43**, 131 (1927); **47**, 258 and 357 (1929).

10. H. G. Bungenberg de Jong and H. R. Kruyt, Proc. Roy. Acad. Amsterdam **32**, 849 (1929); Koll. Z. **50**, 39 (1930), and numerous papers of H. G. Bungenberg de Jong and his pupils in Biochem. Z. since vol. **212** (1929).

11. D. R. Briggs, J. Phys. Chem. **34**, 1326 (1930).

CHAPTER XIV

PROTEIN SOLS

73. Amino-acids in True Solution.—In this chapter it will be shown that the behavior of protein sols is in complete accord with the general stability conditions developed in the previous chapter. The line of reasoning developed and the conclusions drawn will be considerably at variance with the customary trend hitherto followed in textbooks of physiological chemistry. As stated on page 190, these texts usually consider protein sols as solutions of electrolytes; i.e., as systems in which the proteins are molecularly or ionically dispersed.

Proteins are known to be substances which, in the language of organic chemistry, behave like amino-acids. Their molecular size is, as a rule, unknown, and thus may be imagined to agree with the dimensions of particles in true colloidal dispersion. This trend of thought will be discussed later (p. 207); but for the present we postulate that protein sols are colloidal systems. In fact, they are *the classical examples* of colloids; hence, they consist of polymolecular particles, and the chemical processes in which they take part occur at the boundary of these particles, so that here, as elsewhere, we are dealing with boundary phenomena. In the preceding chapters it was found that what happens in the boundary is either adsorption pure and simple or electro-adsorption with capillary electrical effects. In the case of protein sols, these phenomena also play an important rôle, and the knowledge gained from amino-acids in true solution—for instance, from aminobenzoic acid—will be valuable in helping us to understand the interaction of the molecules on the outside of the particles and the surrounding liquid. Let us consider, therefore, first of all, the properties of amino-acids that are in true solution as amphoteric electrolytes.

An amphoteric electrolyte is one that can split off both hydrogen ions and hydroxyl ions and hence can act either as anion or cation, as is the case, for instance, with aminobenzoic acid. In a strongly acid solution (for instance, HCl) it breaks up chiefly into the following ions:

$$Cl^- + (HNH_2C_6H_4COOH)^+;$$

and in a strongly alkaline solution (NaOH, for instance) into the ions:

$$(NH_2C_6H_4COO)^- + Na^+.$$

Hence, the amino-acid may be in equilibrium with both H ions and OH ions; but these two ions themselves are in equilibrium only when they obey the well-known equation for the dissociation of water:

$$c_{\mathrm{H}^+} \cdot c_{\mathrm{OH}^-} = K_w \qquad (K_w = 0.64 \times 10^{-14} \text{ at } 18°).$$

If we designate the affinity constant of the aminobenzoic acid, when it acts as an acid, by K_a, and indicate its dissociation constant when it acts as an amine by K_b, then the following three equations hold simultaneously for the amino-acid:

$$c_{\mathrm{H}^+} \cdot c_{\mathrm{OH}^-} = K_w \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$c_{\mathrm{H}^+} \cdot c_{\mathrm{R}^-} = K_a \cdot c_R \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$c_{\mathrm{OH}^-} \cdot c_{\mathrm{R}^+} = K_b \cdot c_R \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where c_R is the concentration of the undissociated molecules of amino-acid and c_{R^+} and c_{R^-} the concentrations of its cation and anion.

Since amino-acids are generally more acid than alkaline, we find as a rule that $K_a > K_b$.

If conditions are so arranged that $c_{\mathrm{R}^+} = c_{\mathrm{R}^-}$, there are as many positively charged ions of amino-acid as there are negatively charged ones (besides the so-called "Zwitter" ions); therefore, an electric current cannot produce any visible displacement of amino-acid in this solution. This condition, in which there is no displacement by an electric current, is called the *iso-electric point* of the amino-acid.

For $c_{\mathrm{R}^+} = c_{\mathrm{R}^-}$, we can derive, from equations (2) and (3):

$$\frac{c_{\mathrm{H}^+}}{c_{\mathrm{OH}^-}} = \frac{K_a}{K_b}. \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Since $K_a > K_b$, the concentration of the H ions must also be greater than that of the OH ions at the iso-electric point; hence the latter lies in a slightly acidified solution. Furthermore, we can readily infer that at the iso-electric point the dissociation of the amino-acid is a minimum. It is self-evident that this condition is reached in weakly acid solution, since the dissociation of the weak amino-acid must be forced back by hydrogen ions introduced from the outside. This conclusion is also obtained by solving equation (1) for c_{OH^-}, $c_{\mathrm{OH}^-} = \frac{K_w}{c_{\mathrm{H}^+}}$ and substituting this value in equation (4):

$$c_{\mathrm{H}^+}{}^2 = \frac{K_a K_w}{K_b}.$$

Consequently, the hydrogen-ion concentration of the iso-electric point is determined by the three equilibrium constants, and this value is independent of the *concentration* of the amino-acid; in other words, the iso-electric point lies at the same hydrogen-ion concentration, no matter whether we have a hundredth-normal or a tenth-normal solution of the amino-acid.

Amino-acids react with alkalies, forming salts of the type: $\mathrm{R}^{\mathrm{COONa}}_{\mathrm{NH_2}}$; whereas with acids they form acid salts of the general type: $\mathrm{R}^{\mathrm{COOH}}_{\mathrm{NH_2HCl}}$. With neutral salts they react slightly or not at all, for the simple reason that they are weak acids and hence are not affected by neutral salts of strong acids and bases, except for the possible forcing back of ionization by a common ion.

74. Colloid Character of Protein Sols.—One may ask: Are protein sols systems like those discussed in the previous section? No doubt, they contain molecules of amino-acids, and certain electrical phenomena can be as well explained from the viewpoint developed in Sec. 73 as from the concept that a protein particle is not a single molecule but a polymolecular unit, subject to cataphoresis, for instance.

If the protein in a sol is displaced by an electric current flowing toward the anode, it is possible that we are dealing with dispersed anions of protein or with negatively charged colloidal particles. In either case there will be a displacement of the protein toward the anode.

Nevertheless, both in the previous section and in the preceding chapter, several arguments were advanced in favor of the second conception. In Sec. 76, other considerations pointing in the same direction will be mentioned. Furthermore, certain inferences drawn from Sec. 73 do not hold for protein systems. For instance, in discussing equation (4) we saw that the iso-electric point of amino-acids in *true* solution lies at a certain hydrogen-ion concentration which is independent of the concentration of the solution. From the researches of Pauli and Samec[1] it appears that this is *not* the case for protein sols since the hydrogen-ion concentration of the iso-electric point varies with the concentration of the protein. Hence, the conclusion is reached that a colloidal protein particle consists of a large number of molecules, some of which are are found on the outside of the particle while others are inside. The molecules of the periphery are in a position to interact with their surroundings and determine the electrical condition of the particle. The statements made in Sec. 73 about amino-acids are more or less valid for the molecules on the outside of the particle. Depending on the state of acidity or alkalinity of the medium, the ionization of the molecules in the boundary will be determined by the group $\mathrm{RNH_3^+} \mid {}^{-}\mathrm{Cl}$ or by the group $\mathrm{RCOO^-} \mid \mathrm{Na^+}$. Furthermore remembering that at the interface the electrically polar groups orient themselves at right angles to the boundary whenever possible (see p. 41) we realize that the charge of the particle is governed by the hydrogen-ion concentration of the medium. In Fig. 93 is sketched the condition of a particle, first, for a hydrogen-ion concentration greatly in excess of that belonging to the isoelectrical point (Fig. 93 *a*), and second, for a slight hydrogen-ion concentration (Fig. 93 *c*). These sketches express the idea that the colloidal particle is either positive or negative, depending on the hydrogen-ion concentration, and also that there is one hydrogen-ion concentration at which the particle is neither positive nor negative (Fig. 93 *b*). Using the symbols first employed on page 107, we can represent the three possibilities of Fig. 93, in the following manner:

$$\boxed{\text{protein, H}_2\text{O}}\ \mathrm{RNH_3^+ + Cl^-} \qquad \boxed{\text{protein, H}_2\text{O}}$$
$$\boxed{\text{protein, H}_2\text{O}}\ \mathrm{RCOO^- + Na^+}.$$

The investigations of Pauli, Loeb, and others have shown, for instance, that gelatin does not move in a cataphoretic tube when the hydrogen-ion concentration of the intermicellar liquid corresponds to $P_H = 4.7$. For pure water $P_H = 7$. According to the statements of Sec. 73 we have minimum dissociation for a value of $P_H = 4.7$; hence, the number of electro-polar groups is a minimum for this concentration and we have as many $-COONa$ groups as there are $-NH_3Cl$ groups. In other words, the charge of the particle is zero. We also find, in accord with previous statements, that the iso-electric point lies at a slight concentration of acid.

It is obvious that a natural protein which has been subjected to dialysis against pure water for a considerable time changes into

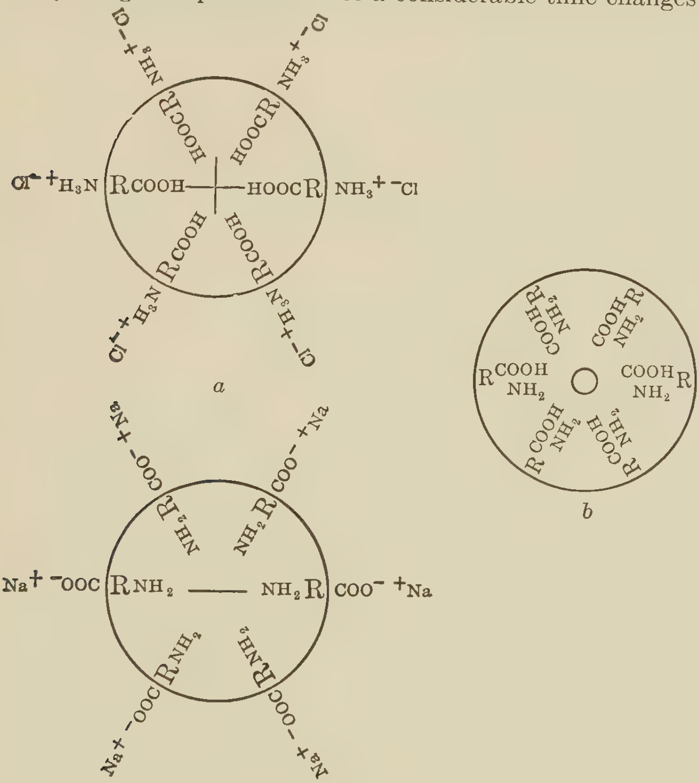

FIG. 93.

a colloid with an intermicellar liquid of hydrogen-ion concentration $P_H = 7$. Years ago, PAULI had already found that the electric charge of proteins decreased considerably on prolonged dialysis. Nevertheless, we often meet, in chemical literature, with the incorrect statement that one can obtain neutral protein in this manner. PAULI himself stated that prolonged dialysis produces a protein sol that is *slightly negative.* This is only natural since we are here on the negative side of the iso-electric point. Strictly neutral protein is obtained by dialyzing against water containing so much acid that the concentration of the iso-electric point is just reached. LOEB found that one can best remove all ash constituents by the use of such a liquid. It should be remarked, however, that even if adsorbed constituents are removed, others are always introduced by the process of displacement adsorption. Hence, we cannot confirm LOEB's statement that gelatin treated with an acid solution of $\frac{1}{1024}$ normal hydrochloric acid or $\frac{1}{128}$ normal acetic acid is completely free from substances that are not gelatin. If one has used hydrochloric acid, the presence of chlorine, which has entered into the gelatin by displacement, can readily be detected.

This idea of the structure of proteins is completely in line with the considerations of the preceding chapter and explains the behavior of protein sols satisfactorily.

Let us discuss, first of all, the viscosity of a gelatin solution as a function of the hydrogen-ion concentration. LOEB made an unusually extensive study of this relationship. It is to his credit that he paid particular attention to the hydrogen-ion concentration of the intermicellar liquid and did not confine his investigations to the concentration of the added acids and bases. In the course of his researches, he gradually dropped his early view that gelatin solutions were true electrolyte solutions; and the present writer is convinced that, had his untimely death not interrupted his work, he would before long have arrived at the theory that is here propounded. His last experiments on the cataphoretic velocity of gelatin pointed clearly in this direction. Probably he would have been forced to retract erroneous statements regarding colloid chemistry made in previous years. As a matter of fact, he had already deserted his original viewpoints a number of times in the period from 1918 to 1923.

The general character of the change in the viscosity with the variation in the hydrogen-ion exponent is indicated in Fig. 94. At the iso-electric point the charge is zero, and, since the electro-viscous effect is necessarily a minimum at this point, the viscosity must increase both by an increase and by a decrease of the hydrogen-ion exponent. The increase in viscosity from the iso-electric point onward must, therefore, be primarily caused by the electro-viscous effect. The fact that this increase gives rise on both sides to a maximum is in full accord with previous statements concerning capillary electrical processes (see p. 85), i.e., that all charging effects are maintained up to certain maximum values, to be followed by a subsequent decrease. Similar behavior is exhibited by the viscosity curve drawn in Fig. 94.

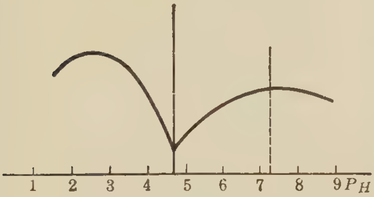

Fig. 94.

It will be shown presently that hydration is also dependent on the electric charge and that there are consequently *two* factors which affect the viscosity.

In this trend of thought, the hydrogen ion, as such, does not play a unique part. In Loeb's opinion, this ion was all-important; he thought that only an ion which determines the chemical behavior of protein could produce an effect. However, boundary charges are modified not only by chemical reactions in the interface but also by adsorption of oppositely charged ions, particularly of polyvalent ions. Kruyt and Tendeloo[2] have recently found that the course of the viscosity curve drawn in Fig. 94 is not exclusively governed by hydrogen ions. For instance, if we choose a gelatin sol with $P_H = 4.4$, which is positively charged and represented by a point to the left of the isoelectric point, we shall find that addition of $K_3Fe(CN)_6$ causes a lowering of the viscosity due to the trivalent anion. At a concentration of $1\frac{1}{4}$ milli-equivalents per liter a minimum value is reached. At higher concentration the viscosity again increases; yet under all these circumstances the P_H remains unchanged. Hence, we can reach the iso-electric point either by establishing a P_H of 4.7 in the medium or else by bringing it up to a P_H of 4.4 by the addition of $1\frac{1}{4}$ milli-equivalents of $Fe(CN)_6^{---}$. In fact, the same effect is obtained when the P_H is made equal to 4.9 and 0.2 milli-equivalent of $[Co(NH_3)_6]^{+++}$, i.e., the cation of luteo-cobalt chloride, is introduced. This investigation demonstrates convincingly that neither the H ion nor the OH ion occupies a unique position, but that simply the general action of cations and anions is involved. This action merely becomes somewhat more pronounced whenever there is a special chemical relation between the ion and the material of which the dispersed particles consist (H ion and protein for instance).

Concerning the effect of alcohol on the stability of gelatin sols, Loeb found that the sol is extremely sensitive to alcohol at the hydrogen-ion concentration of the iso-electric point, a result which agrees with statements made in the foregoing pages. On page 192 attention was called to the dehydrating character of alcohol and the rôle it plays in removing one of the stability factors. When a sufficient amount of alcohol is added, the sol can only exist insofar as is consistent with its electric charge. The latter being at its minimum for the iso-electric point, it is evident that very little dehydration is required to deprive the sol entirely of its stability. Figure 95 shows the so-called alcohol numbers plotted as ordinates against the hydrogen-ion exponent as abscissa. By alcohol number, Loeb means the number of cubic centimeters of alcohol which must be added to 5 cc. of sol in order to produce flocculation.

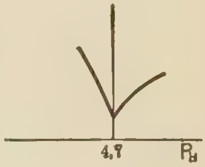

Fig. 95.

The iso-electric point is also a minimum for the electrical conductance of the sol. It is obvious that the conductance is greater the higher the potential of the double layer, i.e., the more polar groups constitute the double layer. It goes without saying, therefore, that the iso-electric point represents a minimum in the electrical conductance.

The minimum osmotic pressure at the iso-electric point will be taken up in the next chapter (see p. 224).

Loeb laid particular emphasis on the fact that the effect of different acids on protein solutions is perfectly stoichiometric; he used this as a strong argument in favor of the molecularly dispersed nature of protein sols. The author is inclined to think this view incorrect because this is also true of polymolecular particles, in which only the molecules of the boundary layer react. It is evident that these boundary molecules will react proportionately to their number. Hence, the concept here set forth explains perfectly the stoichiometric relation to which Loeb called special attention.

Furthermore, there is another fact, totally incomprehensible in Loeb's theory, but readily understood from the point of view of this discussion, viz., the great difference in the properties of various gelatin sols. If they were all molecularly dispersed, their condition, and hence their properties, would be completely defined. But, precisely because of the poly-dispersity of the systems, their ultimate properties depend entirely on the incidental circumstances under which the sols are prepared. For these reversible colloids, the conditions of peptization are really simple; but the final product is quite sensitive to small changes in the method of preparation, such as previous imbibition, temperature of dissolving, speed of warming, stirring, etc. In Loeb's experiments, only one gelatin solution was used for each series, and consequently we do not notice these differences. One would err, however, in assuming that two 1 per cent solutions of gelatin, for instance, were stoichiometrically on a par. Experimental evidence will immediately nullify his idea. Loeb's work could, at best, only prove that for a given gelatin solution one and the same number of

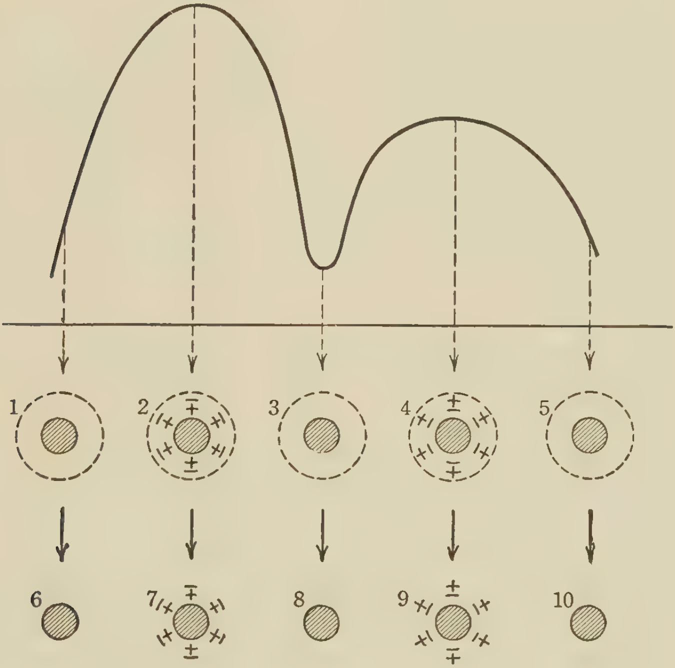

Fig. 96.

molecules (viz., those in the boundary layer of the particles) is active in various reactions; it could by no means verify the statement that *all* gelatin molecules present in solution react. Moreover, HOFFMAN and GORTNER [3] have shown that even the former simple relation does not exist.

To complete this discussion, a sketch of the stability conditions in a protein sol of the gelatin type is given. Figure 96 brings out clearly the respect in which a gelatin sol differs from a sol of the agar-agar type (Fig. 92, p. 200) where the charge is not determined by the amino-acid character of the constituents of the boundary layer. Drawings 1–5 (Fig. 96) represent the hydrated particle at different hydrogen-ion concentrations. If 3 indicates the uncharged particle at the iso-electric point, 2 represents the condition in a more acid medium, and 4 the condition in a more basic one. Excess of acid causes a lowering of the charge, as shown in 1; while excess of alkali produces the same effect, as indicated in 5. These five sketches agree with the viscosity curve of Fig. 94.

If alcohol is added to the sol in these various conditions for the purpose of dehydration, we obtain the conditions designated by the numbers 6–10, which are readily understood. In cases 7 and 9 a stable suspensoid is formed. In cases 6, 8, and 10 flocculation takes place, since neither of the two stabilizing factors, i.e., neither charge nor hydration, is left.

Figure 96 illustrates, therefore, all possibilities of stability and flocculation in a system of the gelatin type, based on the general considerations developed in the preceding chapter. It shows that this theory thoroughly elucidates the dynamics of a protein sol.

Coacervation phenomena, discussed in Sec. 72, may of course occur as intermediate stages. For the sake of simplicity these are omitted from the figure.

75. Sols of the Casein Type.—In the foregoing discussion it has been steadily maintained that a sol can exist either by hydration alone or solely by virtue of its electric charge. However, there are undoubtedly some proteins that are not sufficiently hydrated to be stable by their hydration alone; in such cases a certain ionization of boundary molecules is required to furnish a sufficient charge and make up for the deficiency in stability caused by the defective hydration. An example is casein, which can exist either in an acid or in an alkaline solution, but does not dissolve in water, with the consequence that the sol ordinarily flocculates when neutralized.

In general, we can represent the conditions by the sketches reproduced in Figs. 97 and 98, where the potential of the double

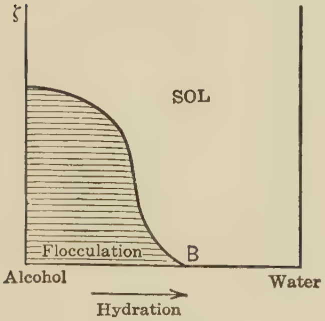

FIG. 97.

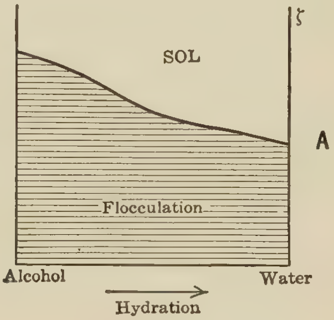

FIG. 98.

layer is plotted as ordinate. The concentration ratio alcohol-water (not the hydration itself) is chosen as abscissa.

A gelatin sol (Fig. 97) is stable in water for any charge, even a zero charge. When, however, an uncharged sol is dehydrated, flocculation occurs at the point *B*, and we enter into the cross-hatched precipitation zone. For a higher charge stronger dehydration is required to bring about flocculation, as is also shown in the figure.

Figure 98 illustrates the behavior of casein in the same manner. This system is stable in water only when the charge of the boundary layer exceeds that of the point *A*. Dehydration by alcohol increases the possibility of flocculation, as is indicated schematically in the figure.

A comprehensive study [4] has shown that casein does behave as an emulsoid sol, but that as such it is far behind agar-agar sols and gelatin sols in lyophile properties. It might be considered a sol in which suspensoid properties predominate, and hence its place would seem to be midway between a typical suspensoid sol and a typical lyophile sol. It is similar in behavior to tin oxide (*cf.* p. 104) which can likewise be peptized in an alkaline or in an acid medium; tin oxide sol is, therefore, in a way a suspensoid with electrical properties resembling those of proteins. In fact, like proteins, tin oxide also shows amphoteric properties to a certain degree.

76. Conclusions.—Briefly summarizing our ideas regarding the stability of suspensoids and emulsoids, we arrive at the following conclusion, which is best illustrated by means of four characteristic sols: (1) gold sol, (2) tin oxide sol, (3) agar-agar sol, (4) gelatin sol.

The stability of these sols is dependent on the electric charge, on hydration, or on both. In the case of the first two sols there is practically no hydration; they are suspensoids, the stability of which is solely a function of their electric charge. The last two sols can exist on the strength of their considerable hydration alone, although they are generally stabilized by both charge and hydration.

Between sol 1 and sol 2 there exists a difference already extensively discussed on page 106. The gold atoms in the periphery of the gold particle are not able to form a double layer of their own accord, but require an outside peptizing electrolyte in order to obtain a charge. The flocculation of such a sol is almost in accordance with FREUNDLICH's theory, discussed on page 71. The tin oxide sol, however, has a double layer, the inner coating of which is furnished by the sol itself. Since this inner coating may be positively or negatively charged, depending on the stabilizing electrolyte, two kinds of sols are possible.

About the same difference exists between the two emulsoid sols mentioned above. The carbohydrate agar-agar is in itself little suited to the formation of a double layer. Traces of an electrolyte (possibly derived from the ash content) build up the double layer, and the phenomena of discharge are generally in line with the theory of FREUNDLICH. The gelatin sol, on the other hand, possessing ionogen molecules, can form a double layer either in an acid or in an alkaline medium, thus greatly resembling the tin oxide sol.

Hence, there is this difference between sols 1 and 2, and likewise between sols 3 and 4; viz., that sols 1 and 3 derive their double layers from absolutely extraneous constituents whereas in the second and the fourth cases one constituent of the double layer originates in the particle itself.

We thus see that our considerations have led to a generalized conception of the stability of colloids, which is applicable to both suspensoids and emulsoids. In spite of the great diversity in properties of colloidal substances there has been developed a line of reasoning which condenses the broad domain of colloid chemistry to a comparatively small number of fundamental concepts. We have been enabled to carry through this idea by means of a detailed discussion of four extreme cases. In Sec. 92 some space will be devoted to a few other colloids which lie between these extreme cases; for here, as elsewhere, our attention is fixed, first of all, on the extreme cases even though it is fully realized that there exist numerous intermediate ones.

77. Special Properties of the Gelatin Sol.—The gelatin sol has frequently been used as the most typical lyophile sol, although, as frequently stated in the foregoing pages, the agar-agar sol represents a much simpler type and hence is to be preferred as the classic example of this group of colloids.

Gelatin, however, has a number of peculiarities which make it very remarkable.

In the first place, the term " gelatin " is indefinite in meaning since the properties of the decomposition products of collagen vary all the way from those of hard gelatin to those of glue. Evidently, we are confronted by a gradual breakdown of the constituents of collagen in successive steps. Any sample of gelatin will be found to be a mixture of these various decomposition products.

There is, however, one very striking property of gelatin that is not possessed by any other protein solution: this is the equilibrium reaction which, below 50°, takes place at a slow but quite perceptible rate. This phenomenon makes itself apparent in various ways, most characteristically in the mutarotation which has been carefully studied by Smith.[5] The polarization of a freshly prepared solution changes slowly with time, reaching an end value which depends on the temperature. Another method of studying this phenomenon was followed by von Schröder[6] for hydrosols of gelatin, and by Arisz[7] for glycerosols of gelatin. They found that the viscosity is a function of the previous history, in other words, of the temperature at which the sol has been kept and the speed with which it has attained its final temperature.

This special property of gelatin is probably not of a colloid-chemical nature but belongs to a reaction occurring inside the molecules of the dispersed particles. The phenomena of mutarotation have been fully investigated for molecularly dispersed systems,[8] for instance, for glucose, while systems with dynamical isomers [9] correspond entirely to those studied by ARISZ. Gelatin sols, therefore, are systems of very special properties and it would be a mistake to consider their behavior as characteristic of lyophile sols in general.

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CHAPTER XV

OSMOTIC PHENOMENA

78. Osmotic Phenomena of Colloids.—As a physico-chemical quantity, osmotic pressure occupies a unique historical position: VAN'T HOFF's theory of dilute solutions took as its starting point the osmotic pressure. This quantity itself appears to play a large part in biological processes, and, although direct measurements of osmotic pressure have been comparatively few in number, it has acquired—rightly or wrongly—a certain historical prestige which gives it a high standing, particularly among biologists.

In the theory of dilute solutions, the osmotic pressure is taken to be proportional to the molecular concentration. When brought in relation to the lowering of the freezing point and the elevation of the boiling point, it furnishes three methods for the determination of the molecular size of dissolved substances. The measurement of the two last-named quantities has given no results at all when applied to colloids. On the other hand, numberless measurements of osmotic pressure have been performed for colloids, especially for proteins. On page 154 the difficulties that must be avoided at the outset were pointed out. Even in the case of systems in true solution, one measurement of the osmotic pressure is not sufficient to give an insight into the number and size of the particles that are osmotically active.

79. Theory of Donnan.—Let us place in an osmometer a substance such as Congo red, which is ionized into the Na ion and the Congo red ion, the first of which passes freely through a collodion membrane while the second cannot pass. DONNAN, in 1911,[1] propounded a theory which explains the effect of added electrolytes on the osmotic pressure, even when these electrolytes themselves can pass freely through the membrane.

As an example, DONNAN takes an aqueous solution of Congo red in the presence of sodium chloride.

Let us employ the subscript i for concentrations inside the osmometer and o for those outside. It is obvious that free ions cannot pass the membrane; each Na^+ ion must move as one of a pair of which the other member is a Cl^- ion; since otherwise these ions would set up powerful electrostatic forces which would prevent diffusion. The frequency with which a sodium and a chlorine ion, inside the osmometer, simultaneously strike a unit area of the membrane depends on the product of the ionic concentrations, viz., $[\mathrm{Na}^+]_i \times [\mathrm{Cl}^-]_i$. Likewise, the chance of a sodium and a chlorine ion striking a unit area of the membrane from the other side, is proportional to the product $[\mathrm{Na}^+]_o \times [\mathrm{Cl}^-]_o$.

Equilibrium will be established only when the transfer of paired ions per unit time is the same in both directions, whence:

$$[\mathrm{Na}^+]_i \times [\mathrm{Cl}^-]_i = [\mathrm{Na}^+]_o \times [\mathrm{Cl}^-]_o. \quad . \quad . \quad . \quad (1)$$

It follows, therefore, that the product of the concentrations of the Na^+ and Cl^- ions has the same value on the inside and on the outside. The Na^+ ions inside the osmometer are derived not only from the salt but also from the Congo red, a fact which complicates the sodium chloride equilibrium on both sides of the membrane.

Let us indicate the initial state of affairs by the left-hand side of the subjoined scheme, where the symbols to the left of the vertical line designate the liquid inside the osmometer, and those to the right the outside liquid. Congo red is represented by the symbol NaR. The initial concentrations are assumed to be all the same, viz., c.

At the outset: At equilibrium:

$$\begin{array}{cc|cccc|cc}
\mathrm{Na}^+ & \mathrm{R}^- & & & & \mathrm{Na}^+ & \mathrm{R}^- & & \\
c & c & & & & c & c & & \\
 & & \mathrm{Na}^+ & \mathrm{Cl}^- & \rightarrow & & & \mathrm{Na}^+ & \mathrm{Cl}^- \\
 & & c & c & & & & c+x & c+x \\
\mathrm{Na}^+ & \mathrm{Cl}^- & & & & \mathrm{Na}^+ & \mathrm{Cl}^- & & \\
c & c & & & & c-x & c-x & &
\end{array}$$

From equation (1) it will be evident that, at the start, there are too many sodium ions inside the osmometer, hence some salt moves out, the loss in concentration being represented by x. The final state of affairs, as shown on the right, leads then to the following relation, obtained by substituting the right values in equation (1):

$$(2c - x) \times (c - x) = (c + x)^2,$$

or:

$$2c^2 - 3cx + x^2 = c^2 + 2cx + x^2,$$

whence:

$$x = \tfrac{1}{5}c.$$

There will be equilibrium when the concentration of the sodium chloride is $\frac{4}{5}c$ on the inside and $\frac{6}{5}c$ on the outside.

Furthermore, we count the number of osmotically active particles present, and find that there are $3\frac{3}{5}\ cN$ particles inside the osmometer and $2\frac{2}{5}\ cN$ particles outside (N = Avogadro's constant).

If we did not follow this line of reasoning, but adopted the viewpoint that the presence of the salt is immaterial, since it can pass freely through the membrane, we should have

$$\pi = 2cRT,$$

whereas Donnan's theory plainly shows that the osmotic pressure, π, is equal to $(3\frac{3}{5}-2\frac{2}{5})cRT$, or $1\frac{1}{5}cRT$.

Calculations based upon the above theory lead, therefore, to a value for the osmotic pressure 40 per cent lower than that obtained by a haphazard application of the law of van't Hoff.

With other concentrations of Congo red and sodium chloride, using the same osmometer system, we obtain the results reproduced in the table below:

TABLE XXV

Initial Concentrations			Final Concentrations		Final $\frac{\pi_D}{\pi_H}$
NaR_i	Total NaCl	Ratio $\frac{c_1}{c_2}$	Per cent $NaCl_i$	Ratio $NaCl_o : NaCl_i$	
0.01	1	0.01	49.7	1.01	0.50
0.1	1	0.1	47.6	1.1	0.52
1	2	0.5	40	1.5	0.60
1	1	1	33	2	0.67
1	0.1	10	8.3	11	0.92
1	0.01	100	1	99	0.99

From this table, taking for instance the last row, we see that the salt is almost exclusively in the outside liquid. One might be inclined to say that the membrane is *impervious to the salt.*

If we calculate the ratio between the osmotic pressure according to VAN'T HOFF's well-known law and the osmotic pressure as computed by DONNAN, we find the values given in the last column of Table XXV at the corresponding ratios of concentrations used.

The ratio of the osmotic pressures as calculated by DONNAN's and VAN'T HOFF's methods is mentioned as $\frac{\pi_D}{\pi_H}$.

It might be thought that these complications occur *only* when the diffusible salt has an ion in common with a substance of the type of Congo red. This is, however, not the case. With an initial and a final condition in the osmometer and surrounding liquid as represented by the scheme:

$$\begin{array}{cc|cc} \mathrm{Na}^+ & \mathrm{R}^- & \mathrm{K}^+ & \mathrm{Cl}^- \\ c_1 & c_1 & c_2 & c_2 \end{array} \rightarrow \begin{array}{cc|cc} \mathrm{Na}^+ & \mathrm{R}^- & \mathrm{K}^+ & \\ c_1-z & c_1 & c_2-x & \mathrm{Cl}^- \\ \mathrm{K}^+ & \mathrm{Cl}^- & \mathrm{Na}^+ & c_2-x+z \\ x & x-z & z & \end{array}$$

equation (1) may be written in the following form:

$$\frac{[\mathrm{Na}^+]_i}{[\mathrm{Na}^+]_o} = \frac{[\mathrm{K}^+]_i}{[\mathrm{K}^+]_o} = \frac{[\mathrm{Cl}^-]_o}{[\mathrm{Cl}^-]_i} = \frac{c_1 + c_2}{c_2}.$$

A computation of equilibrium concentrations gives the figures reproduced in Table XXVI.

TABLE XXVI

$\frac{c_1}{c_2}$	$\frac{c_1+c_2}{c_2}$
1	2
10	11
100	101

80. Application to Colloids.—In the preceding discussions we were dealing with an electrolyte one ion of which could pass the membrane freely while the other was unable to do so. The further development of the theory, however, is entirely independent of these conditions. The theory is based on the fact that through some cause or other a difference in concentration is established on opposite sides of the membrane. Regardless of the cause of this difference in concentration, the theory leads to the perfectly general statement that the ionic products inside and outside the osmometer must be the same.

Whenever we have in the osmometer a colloid in the presence of a peptizing electrolyte, the stabilizing ions are undoubtedly attached to the particles while the other ions move more or less freely in the intermicellar liquid (diffuse double layer). Moreover, part of the electrolyte is not adsorbed at all and will be distributed between the inner and the outer liquid. The case for which equation (1) on page 220 holds is, therefore, present, although the substance involved (the colloidal micells) is by no means an electrolyte of the Congo red type.

Loeb [2] made numerous osmotic measurements, using the gelatin sol, and with the aid of a line of reasoning advanced by Proctor and Wilson,[3] he compared the results obtained with the data derived from an application of Donnan's theory. The agreement was obviously very good since his case was the one just mentioned. Loeb inferred, quite erroneously, that his system belonged to the type exemplified by Congo red, i.e., an electrolyte in true solution one ion of which—viz., the gelatin ion—cannot pass through the membrane. General objections to this view have already been developed. Here, too, we are justified in rejecting the conclusiveness of the arguments in the field of osmotic measurements for the simple reason that the agreement with Donnan's theory holds just as well for a colloid in adsorption equilibrium with a peptizing electrolyte as it does for an electrolyte of the Congo red type.[4]

81. Measurements.—From the preceding discussion it will be clear that little importance can be attached to measurements of osmotic pressure for the determination of the particle size. The unavoidable, ever-present quantities of peptizing electrolytes and the resulting deviations from the law of van't Hoff render any computation illusory, while, on the other hand, our knowledge of the concentration of the electrolytes present in solution is not always sufficiently exact to make possible a proper use of DONNAN's theory. The measurements of DUCLAUX,[5] BILTZ,[6] LILLIE,[7] and many others leave us completely in the dark with respect to the size of the particles in the sols. The methods discussed on page 187 will bring us to a knowledge of the size of the particles much sooner than will osmotic measurements, however important the latter may be for studying molecularly and ionically dispersed systems.

Meanwhile, it may be well to mention at this point an example which has attracted considerable attention on account of the apparent agreement of results obtained by different methods. The substance referred to is haemoglobin. LILLIE derived a molecular weight of 16,000 from osmotic measurements. The empirical formula of hæmoglobin is, supposedly,

$$C_{758}H_{1203}O_{218}N_{195}S_3Fe.$$

Assuming that only one atom of iron occurs in the molecule, we find a value of 16,666 for the molecular weight. From the amount of CO which is taken up by hæmoglobin, we find, on the basis of one mole of CO to one mole of the substance, a molecular weight equal to 16,721. Measurements of the constant of diffusion give the value of 20,000. Osmotic measurements by ROAF led to the higher value of 32,000.

Although these figures show concordant results insofar as the order of magnitude is concerned, the author is inclined to think that the agreement is a lucky coincidence. One has to bear in mind that the purely chemical facts involved may be equally well explained from the standpoint of adsorption phenomena, and that such explanations are more probable than those based on stoichiometric relations of molecularly disperse systems.

Various investigators (PAULI, LOEB, *et al.*) have found that proteins, gelatin, etc., possess a minimum osmotic pressure at their iso-electric points. This is readily understood from the preceding paragraphs. Let us assume that the system gelatin + HCl has a P_H of 4, for instance. Particles and double layer are then of the type represented by Fig. 93*a*, with a diffuse double layer of Cl ions; some of these move freely and take part in the osmotic equilibrium, for instance, a fraction, α, of their total concentration c_c. When equilibrium is reached the condition is as follows:

Inside the osmometer					*Outside the osmometer*	
$\boxed{\text{gelatin}}$	$H^+ +$	Cl^-	H^+	Cl^-	H^+	Cl^-
	c_c	c_c	i	i	o	o

According to the equation of the Donnan equilibrium, we have:

$$[H]_i \times \left\{[Cl]_i + \alpha c_c\right\} = [H]_o \times [Cl]_o.$$

For $\alpha c_c = 0$, the free HCl must be present in equal concentration inside and outside, and hence the osmotic pressure must be that of the micells alone, viz., practically zero, which is the case at the iso-electric point (*cf.* Fig. 93*b*). The osmotic pressure falls from the low P_H toward the iso-electric point. The same reasoning applies when we start from higher NaOH concentrations toward the iso-electric point (*cf.* Fig. 93*c*); the osmotic pressure is again at its minimum value, or practically zero, when there is no double layer. The equation: $[H]_i \times [Cl]_i = [H]_o \times [Cl]_o$ then indicates that $[HCl]_i$ is equal to $[HCl]_o$, and hence that the osmotic pressure due to the electrolytes present is zero.

82. Membrane Potentials.—In Sec. 79 we saw that the osmotic equilibrium is established by means of an uneven partition of electrolytes between the liquids on the two sides of the membrane. As a result, there is a potential difference between opposite sides of the membrane.

Let us imagine an osmometer in which there exists an equilibrium of the kind discussed in Sec. 79, with an uneven distribution of the chlorine ions in the osmometer and in the outside liquid. On introducing two calomel electrodes, one into the osmometer and the other into the outside liquid, we obtain a concentration element consisting of two chlorine electrodes placed in solutions having different concentrations of chlorine ions; hence we can apply the well-known formula of Nernst:

$$E = \frac{RT}{nF} \log \frac{c_1}{c_2},$$

which gives us, quantitatively, the magnitude of the potential difference between opposite sides of the membrane.

In general, it is possible to compute the potentials thus produced. It is evident that added electrolytes affect these membrane potentials insofar as they change the concentrations of the ions involved.

Wilson, Loeb, and others think that the differences in potential existing between the gelatin particle and the intermicellar liquid are of the nature of these membrane potentials. In other words, added electrolytes would alter the potential in accordance with the equations derived in Sec. 79 and in line with Nernst's formula. This idea differs radically from the one expressed in Chapter XIII, in which the rôle of capillary electrical processes was emphasized. We are confronted here by the confusion between transverse potential differences, ϵ, and tangential potential differences, ζ, discussed in Chapter VI; hence, these membrane potentials cannot furnish an explanation for the electro-stability of lyophile colloids, a fact that was made clear once more by the last experiments of Loeb[8] himself.

83. Abnormal Osmosis.—A transport of liquid has repeatedly been observed to take place, between two liquids separated by a wall, in a direction opposite to the one expected on the basis of osmotic considerations. In such cases of "abnormal osmosis" there is a movement of liquid from the hypertonic toward the hypotonic liquid. It must be admitted that, as a rule, the membrane cannot strictly be called a semi-permeable wall; but, in the large majority of cases in which osmotic phenomena are considered by biologists, these scientists are not at all certain that the walls with which they are dealing are semi-permeable. The question arises: What is the origin of these countercurrents?

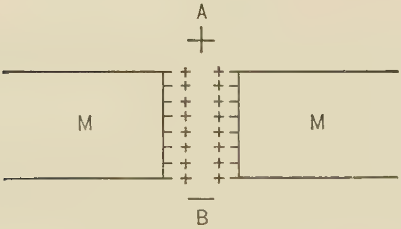

Fig. 99.

Let M (Fig. 99) be a membrane separating two liquids, A and B. In this membrane are capillary openings, one of which is sketched in the figure. When dilute solutions of electrolytes are involved, a ζ potential may be set up at the capillary wall, provided a closed electric current flows through the capillary. To this end, it is necessary that the membrane be not an insulator, since the current must pass through. Generally speaking, the electromotive force of a concentration cell will be set up, as explained in the preceding section. If this E.M.F. is of such a nature that the hypertonic solution, A, is positive with respect to the hypotonic solution, B, and if, furthermore, the wall is negatively charged with respect to the liquid in the capillary, there will occur an electro-endosmotic movement of liquid from the hypertonic toward the hypotonic solution. This phenomenon is abnormal osmosis.

In Chapter V we saw that capillary electrical phenomena in general, including electro-endosmotic movements, disappear whenever the electrolyte concentration is sufficiently increased. For minute quantities, however, the ζ potential is raised. LOEB [9] observed the same behavior in the case of abnormal osmosis; and, what is more, the concentration of maximum electro-endosmosis often coincides with that of maximum abnormal osmosis. On the other hand, mere traces of ions like the Al^{+++} ion, which in very small concentrations removes the ζ charge, likewise eliminate the phenomenon of abnormal osmosis.

A great number of widely differing explanations are found in the literature. In recent years SCHREINEMAKERS [10] has made a thorough investigation of the problem. He arrives at the conclusion that abnormal osmosis is not at all an abnormal phenomenon but a normal one. In fact, in most cases a movement of liquid from the hypertonic to the hypotonic solution must be considered to be a normal equilibrium process. Even in those cases where the process is not one of equilibrium several explanations can be given.[11]

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CHAPTER XVI

GELS

84. Gelatinizing.—Gelatinizing is a well-known phenomenon which may be readily observed with the aid of a gelatin sol. When, for instance, 4 g. of gelatin are dissolved in 100 cc. of water and then allowed to cool, it is noticed that the sol solidifies at room temperature to a solid gel. Gelatinizing, therefore, represents the solidification of the whole system, i.e., of both dispersion medium and dispersed substance, into one apparently homogeneous, solid mass. Macroscopically, *gelatinizing* differs from *flocculation* by the fact that dispersion medium and dispersed phase solidify together, whereas flocculation shows a visible separation of the two. (*Cf.* p. 7).

Agar-agar gelatinizes by a decrease in temperature in the same manner as gelatin; but, in addition to these phenomena of *temperature-gelatinizing,* there are others in which *electrolyte-gelatinizing* occurs, as with the sols of aluminium oxide, cerium dioxide, and silica. These sols gelatinize almost immediately on the addition of a sufficient amount of electrolyte.

Table XXVII gives the electrolyte concentrations required to gelatinize these three sols in a definite time. Although the criterion is chosen somewhat differently for each of the sols used, it is evident from the table that the necessary quantities are related to the valence of the oppositely charged ion; hence, there is, as far as the electrolyte action is concerned, a distinct parallelism between gelatinizing and flocculation. This fact at once suggests that gelatinizing may be merely the flocculation of strongly hydrated particles. In that case, we might represent the gel as a coagulum of hydrated particles which, moreover, hold a large amount of water enclosed between the coagulated flakes. The fact that gel formation occurs only with lyophile sols is brought out in a peculiar way with the aid of the sols of cerium dioxide (CeO_2). Two different kinds of sols can be prepared.[4] By dialyzing ceriammonium nitrate ($Ce(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$), one obtains a sol that is strongly hydrated, as shown by its viscosity. The gelatinizing of this sol is indicated in Table XXVII. When the sol is heated for some time at 100°, the relative viscosity at room temperature is lowered to about unity, and the lyophile character of the sol is apparently destroyed. The addition of electrolytes no longer causes gelatinizing, but results in ordinary flocculation.

TABLE XXVII

Al_2O_3 [1] positively charged		CeO_2 [2] positively charged		SiO_2 [3] negatively charged	
Electrolyte	Conc. in millimoles per liter required for gelatination	Electrolyte	Conc. in millimoles per liter required for gelatination	Electrolyte	Conc. in millimoles per liter required for gelatination
NaCl	77	NaBr	5	NaCl	100
KCl	80	$NaClO_4$	5	$\frac{1}{2}Na_2SO_4$	100
K_2SO_4	0.28	NaCl	3.5	$BaCl_2$	15
$K_2C_2O_4$	0.36	Na_2SO_4	0.15		
$K_3Fe(CN)_6$	0.10	Na_2HPO_4	0.16		
$K_4Fe(CN)_6$	0.08				

The question arises: Is not temperature-gelatinizing likewise a coagulation process, i.e., does not gelatinizing *always* consist in flocculation of hydrated particles? The answer to this query was found in an investigation by Bachmann,[5] who studied the process of gelatinizing by means of the ultramicroscope. He prepared a 2 per cent gelatin sol and allowed it to cool in the ultramicroscope. At first, he saw the well-known image of an emulsoid sol, but after a while he noticed the following phenomena:

(1) At the outset, a diffuse light cone was observed, and only a few particles, apparently due to impurities of the sample, were visible.

(2) After three hours, a peculiar scintillation occurred in the light cone, indicating the appearance of visible particles.

(3) Some time later, white submicrons in vigorous Brownian movement were plainly seen.

(4) Gradually, the translatory motion of the particles decreased becoming more and more sluggish, obviously as a result of the increase in the size of the particles.

(5) The particles became so large that the Brownian movement was limited to a swinging motion, translatory movements having apparently come to a standstill.

(6) The whole field was filled with cohering particles without any motion. The gelatinized specimen, therefore, showed an image which was clearly differentiated from that exhibited by coagulated particles (see Fig. 100).

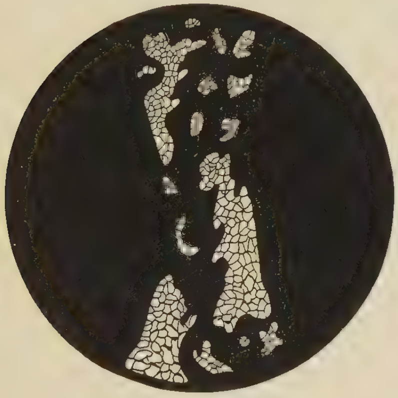


Fig. 100.

It was thus demonstrated that the visible elements consist of submicrons and, possibly, in part of amicroscopic constituents. The light given off is clearly polarized; hence, we might say that the gelatin gel is formed by amicroscopic particles which have joined together to form larger aggregates. These in turn might be distinguishable microscopically (Bütschli).

These observations of Bachmann indicate, therefore, that the process of gelatinizing is accompanied by the union of primary particles into larger aggregates, which is in accord with the line of reasoning set forth previously for electrolyte-gelatinizing. It is, however, rather difficult to imagine in what particular manner the stability factors, viz., hydration and charge, vary during the process described by Bachmann. Concerning the first factor, hydration, it has been found experimentally that lowering of the temperature raises not only the viscosity (η_s) but also the relative viscosity (η_s/η_o); hence, hydration increases when the temperature decreases.

The process of gelatinizing has been investigated, for the most part, by studying the change in viscosity while the transformation from sol to gel takes place. As soon as gelatinizing begins, at a definite temperature, we notice a change in viscosity which increases with the time. Fig. 101 shows, for an agar-agar sol, the viscosity-time curves at different temperatures.[6] Above 40°, these curves run practically parallel to the time axis; at lower temperatures, we clearly notice an increase in viscosity with the time. We must, however, keep in mind that it is only in the first stage of the process that viscosities can really be measured, since the sol, on gelatinizing, no longer follows the law of POISEUILLE (see p. 182).

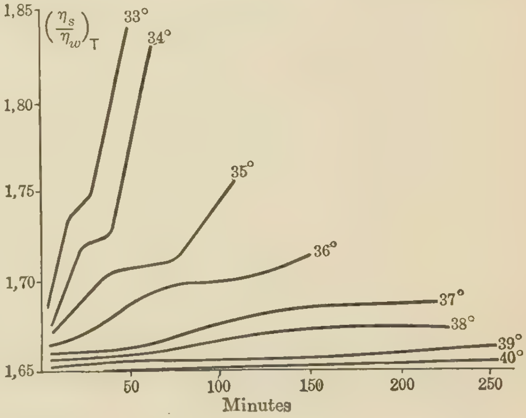


FIG. 101.

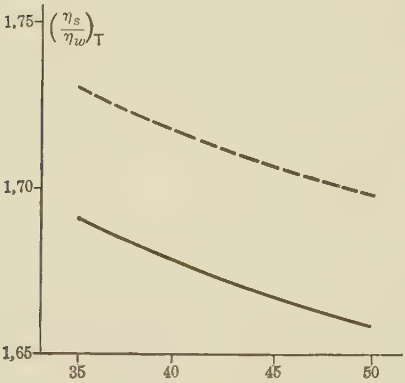


FIG. 102.

When the temperature of an agar-agar sol is lowered, for a few minutes, below 40° and then again raised above 40°, it appears that the viscosity has increased. The broken line in Fig. 102 indicates the properties of such a modified sol as they vary with temperatures above 40°. It is seen in these cases that gelatinizing has permanently increased η. This is readily understood if it be assumed that the agglomerated particles (strongly resembling a coacervation; see Sec. 72) have a larger active volume than the primary particles originally present. Deviation from the spherical shape plays a part, as does also the enclosed water, as is shown schematically in Fig. 103. The cross-hatched portion represents the water surrounding the particles, while the dotted line indicates the viscous active volume. Heating the agar-agar sol at 100°, the temperature at which these sols are prepared, brings about resolution into primary particles, as we have previously noted in the case of reversible colloids (*cf.* p. 11). The fact that a sol gradually increases in viscosity as gelatinizing takes place has led to the idea that the transformation from sol into gel is a completely continuous process. Such a concept, however, is a naïve interpretation of the results of superficial examination. In the first place, elastic properties gradually enter into play in addition to the phenomena of pure viscosity. A gel, therefore, not only has a high viscosity but also possesses elasticity, a property lacking in a sol. Furthermore, the researches of Bachmann have shown that gels are formed by the agglomeration of primary particles into complex particles, so that even in this respect more has happened than is indicated by the simple expression just mentioned.

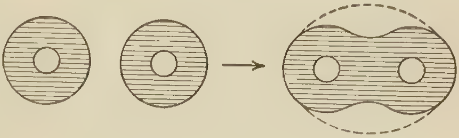
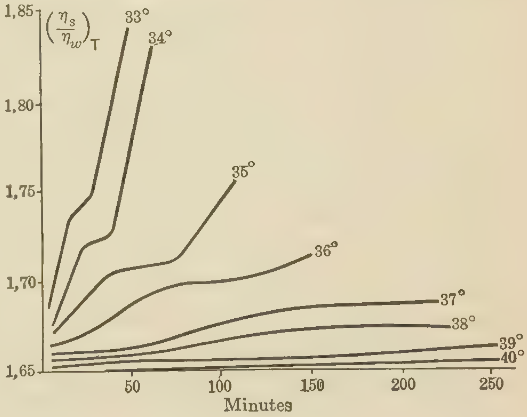


Fig. 103.

The process of gelatinizing might be regarded in still another way, which suggests itself readily. In Fig. 102, we saw that hydration increases as the temperature decreases. One might, therefore, reason as follows: Gelatinizing takes place whenever the particles are so strongly hydrated that no more liquid water is available for the sol condition. Here, too, there are insuperable objections. If this conception were correct, a $\frac{1}{7}$ per cent sol of agar-agar at 35° would contain all of its water as hydrated water, and at 41° we should have reached the limit of existence of such a sol. A $\frac{2}{7}$ per cent sol of agar-agar, containing double the previous amount, could not possibly exist at 41°, which is contrary to experience. The relation between temperature of gelatinizing and concentration is remote; it does exist but it is too slight to be applied to the line of reasoning developed above.

The only satisfactory representation of gelatinizing is, there-



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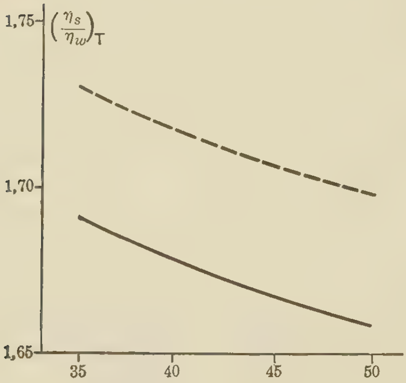

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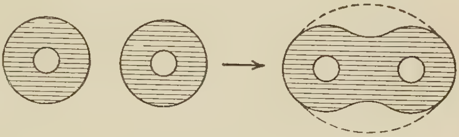

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The only satisfactory representation of gelatinizing is, there-surprising after all, for even a restoration of the former molecular structure does not necessarily involve the same dispersion as before. This requires, perhaps, a greater heat motion.

A change in molecular configuration may, of course, give rise to mutarotation although it is not absolutely necessary. The mutarotation in gelation sols just before the temperature of gelatinizing is reached (*cf.* p. 217), shows that in this case a molecular change certainly precedes gelatinizing. It remains to be seen whether other physico-chemical methods can enable us to demonstrate the occurrence of intramolecular changes in other sols.

BACHMANN'S work has brought out another highly important fact with regard to sols that are so dilute that they do not set to a gel. A gelatin sol of $\frac{1}{4}$ per cent, for instance, does not gelatinize at room temperature. Ultramicroscopically, BACHMANN found that these sols also passed through the three first stages mentioned before. The phenomenon came to an end, however, with a condition in which small flakes floated in the surrounding aqueous medium. This fact is in complete accord with the representation outlined above. The volume of the remaining water is so large that complete coherence of the particles is frustrated, and hence retention of this water within capillary spaces is necessarily out of the question. For this reason, it is well to remember that phenomena of gelatinizing may occur without any macroscopically visible gel formation. This point has already been stressed, on page 182.

85. Thixotropy.—A remarkable change from gel to sol has been studied in recent years by FREUNDLICH[9] and his pupils, first for electrolyte-gelatinizing and later also for temperature-gelatinizing. On the addition of an electrolyte to a concentrated sol of Fe_2O_3, the latter gelatinizes; on shaking the gel, we notice liquefaction, but on standing for a while, the sol, thus formed, again gelatinizes. Numerous other sols, like the Al_2O_3 sol, after gelatinizing, show the same phenomenon, viz., of *changing* their condition when *touched*. This process is, therefore, designated as thixotropy (from the Greek: thixis = touch, and tropein = to change). Gelatin sols, likewise, exhibit this behavior but it is more difficult to observe than in the case of the Fe_2O_3 sol.

We have already seen that the gel is formed by the union of particles on those particular spots where the probability of cohesion is sufficiently great, while for the rest of the surface the conditions of stability are still intact. Obviously, mechanical forces disturb this loose contact but a period of rest restores the normal coagulation.

The peculiar way in which these thixotropic phenomena come to the fore is well illustrated by the following investigation of FREUNDLICH and ABRAMSON.[10] In studying cataphoresis of microscopically visible particles (zinc, quartz, blood corpuscles) in gelatin sols both before and after gelatinizing, they found, strangely enough, that the cataphoretic velocity was practically the same, both in the liquid sol and the solid gel. The cataphoretic movement of the particles apparently causes a thixotropic loosening of the gel structure and the particles move, as it were, through a narrow sol channel which is closed after their passage.

86. Classification of Gels.—The views developed in Section 84 regarding the structure of gels are of fairly general application even though the individual gels differ considerably in properties. For practical reasons, it is desirable to classify the gels into two groups: (*a*) elastic (or swelling); and (*b*) non-elastic (or non-swelling). The phenomena of swelling will be discussed in detail in Sec. 89. When, for example, a gelatin gel is suspended in water it takes up water and increases quite noticeably in volume. When the swollen gelatin is removed, it parts readily with the absorbed water and shrinks. This change in volume on the addition or loss of water is not a property of all gels. The gel of silicic acid, for instance, under certain conditions does not alter its volume when water is taken up or given off. A non-swelling gel is, therefore, one degree simpler than a swelling gel. Hence, in order to obtain an insight into the structure of gels, we shall, first of all, discuss the simpler case and consider the classical example of the silica gel.

87. The Silica Gel.—The gel of silicic acid has been for many years an object of investigation on account of the peculiar changes, both optical and tensimetric, which take place when it is hydrated or dehydrated. J. M. VAN BEMMELEN has carried out elaborate experiments on this gel,[11] while in recent years the investigations performed in ZSIGMONDY's laboratory have led to a good understanding of VAN BEMMELEN's results.

When a silicic acid sol is allowed to coagulate, it forms a gel containing many times more molecules of water than molecules of silica. On placing such a gel in a desiccator over sulphuric acid, we find a gradual decrease in the water-silica ratio. Table XXVIII gives an idea of the change in the outward appearance of the gel during dehydration.

TABLE XXVIII

Number of moles of water to one mole of SiO_2	Property of the Hydrogel
40–30	Gel is so consistent that it may be cut
20	Fairly stiff
12	May be pulverized
8	Somewhat elastic
6	Apparently completely dry

When the water content has decreased still further, i.e., below 6, the investigations become quite interesting. The results obtained by van Bemmelen are reproduced schematically in Fig. 105. The (water) vapor pressures with which the gel is in equilibrium are plotted, as ordinates, against the ratios of water molecules to silica molecules, as abscissae. The diagram is drawn for a temperature of 15°. The vapor pressure of water at 15° is 12.7 mm., as indicated by the horizontal line in Fig. 105. A gel rich in water is in equilibrium with water vapor having a pressure only slightly below the maximum pressure of 12.7 mm. When water is removed, the vapor pressure drops, following the curve WO. At the point O, which is called the *first transition point*, another peculiar phenomenon occurs. Whereas hitherto the removal of water has resulted in a slight diminution of volume, there is no further change in volume once the first transition point is reached. In the second place, when the dehydration is continued beyond O, the decrease in vapor pressure is much less than before; and finally, the gel gradually becomes opaque, whereas previously it has been transparent. This clouding increases continually until the gel is as white as chalk. After that it becomes less and less turbid, so that when the point O_1, the so-called *second transition point,* is reached, the gel is again perfectly clear. On continuing the dehydration by placing the gel successively over more and more concentrated acid, we follow the curve O_1O_2. The small amount of water which is retained at O_2 cannot be driven off at

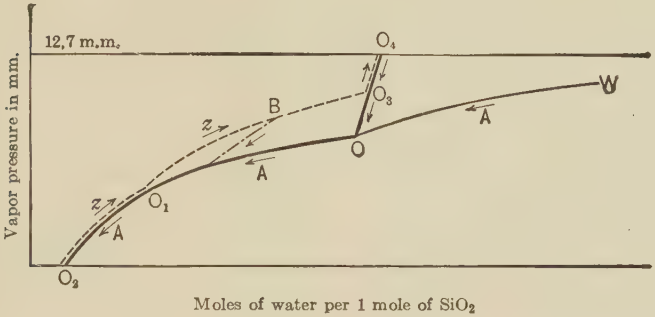

Fig. 105.

lower temperature but requires ignition for its removal. When the dehydration is followed by a rehydration by placing the gel successively in desiccators containing more and more *diluted* sulphuric acid, we retrace, at first, the curve O_2O_1, which is thus seen to be reversible. From the point O_1, on, however, the vapor pressures follow another curve, viz., O_1O_3, which lies entirely above the curve O_1O. Further hydration, from O_3 on, causes a rapid increase in vapor pressure until the maximum pressure is reached (at O_4). If we then dehydrate again, we pass along the path $O_4O_3OO_1$, while the return route is indicated by $O_1O_3O_4$. If the rehydration were interrupted at a point B, and followed by dehydration, we should get the path BA.

This shows the strange cycle in the course of the vapor pressure of the silica gel. One series of curves is followed on dehydration and another set on rehydration, while only the short stretch O_1O_2 is reversible.

The credit for having explained these phenomena and thus having considerably extended our knowledge of gels belongs to Zsigmondy[12] and his pupils. They repeated van Bemmelen's classic experiments in an improved apparatus,[13] confirmed most of his work and, furthermore, explained the facts in the following manner.

Bachmann's investigation, discussed in Sec. 84, indicated that a gel consists of amicroscopic and submicroscopic constituents. A network in which there are only *ultra*microscopic capillaries can be perfectly transparent since the discontinuities are smaller than the wave length of the light. It will only give rise to a Tyndall effect, as is actually the case for gels. The assumption of van Bemmelen (and previously of Bütschli) of a *microscopically* visible honeycomb structure had already been proved to be erroneous by the fact that gels are discontinuous and yet perfectly clear.

Let us see what happens at the first transition point. Before this point is reached the capillaries are filled with water; but at O, where dehydration no longer involves a decrease in volume, any further removal of water must necessarily bring about evacuation of the capillaries. The latter are filled with water under high capillary pressure. The vacuoles resulting from the removal of water appear, on microscopic examination, to originate, not at the outer edge of the gel but on the inside: water is continually sucked through the capillaries toward the outside and vacuoles or air bubbles are formed in the interior, as indicated schematically in Fig. 106.[14] These vacuoles soon reach such dimensions as to be microscopically visible; hence, discontinuities greater than the wave length of light occur and the gel becomes opaque. That the opacity is due to air bubbles is proved by the fact that we actually see the escape of the gas when the gel is immersed in water.

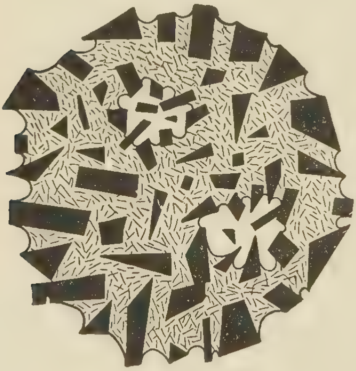

Fig. 106.

On continuing the dehydration, we empty the capillaries more and more, so that at the second transition point they are completely filled with air, apart from the moisture adsorbed by their walls. Thus we have, once more, a system with only *ultra*microscopic discontinuities. The resulting gel is again perfectly clear. The difference between the state of the gel at O and at O_1 is that in the former case the capillaries are filled with water and in the latter they are filled with air.

Dehydration beyond the point O_1 removes the water adsorbed by the gel walls. This is a reversible process and gives to the curve O_1O_2 the character of an adsorption isotherm.

Let us now discuss the process of rehydration. Starting from

O_2, we move *reversibly* along the adsorption isotherm. Beyond O_2 the capillaries gradually become filled with water. It remains to be explained why the vapor pressure is now *greater* than before (during dehydration). There is, in fact, one more question to be answered: Why is the vapor pressure of the water-filled gel not equal to, but lower than that of pure water? These two problems have been solved by ZSIGMONDY by following out one line of reasoning.

It will be remembered (see p. 15) that small drops have a greater vapor pressure than large ones. In general, the vapor tension of a curved surface differs from that of a level surface according to the following formula:

$$\Delta p = \frac{d_D}{d_L - d_D} \cdot \sigma \cdot \frac{2}{R},$$

in which Δp represents the difference in vapor tension between the curved and the flat surface, d_L and d_D are the densities of liquid and vapor, σ is the surface tension, and R the radius of the curved surface. When R is positive, the vapor pressure is increased, as for instance, with drops; when R is negative, there is a diminution of vapor tension. This happens when a liquid is placed in a capillary, as represented schematically in Fig. 107*a*.

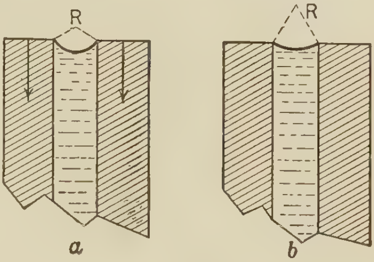

FIG. 107.

We saw previously that the gel has a sponge-like structure with ultramicroscopic capillaries. In each of the capillaries located on the periphery, the water meniscus is concave toward the vapor. This hollow meniscus in the gel capillaries accounts for the fact that, in the experiments illustrated in Fig. 105, the vapor pressure is lower than 12.7 mm. whenever the capillaries are filled with liquid in contact with vapor.

At the point O the condition is reached where the gel attains its definitive form. Between W and O the gel is still subjected to pressure: capillary forces exert an outward pull on the water in the capillary (see Fig. 107*a*) and a corresponding pressure in the opposite direction on the walls; hence, the contraction of the gel goes on from W to O, until at O the gel is in its final form. The capillaries are then filled and the vapor pressure has the value indicated by the above equation. At the start this pressure remains fairly constant, for the reason, previously discussed, that the capillaries on the periphery remain filled and vacuoles are formed only *inside* the gel. This explains the slight slope of the curve to the left of O.

The *higher* vapor pressures on rehydration are due to the fact that during this process the meniscus in each capillary is less curved than in the preceding dehydration. It is well known that the meniscus with which a liquid adheres to a dry wall is less curved than it would be if the wall had been moistened beforehand. This state of affairs is sketched in Fig. 107*b*. A meniscus with greater radius of curvature raises the value of R and hence causes a smaller *lowering* of the vapor pressure; in other words, the vapor pressure is higher than before. Once the point O_3 is reached, the capillaries are completely filled and the addition of more water leads to the formation of a film of water around the whole gel. Immediately the vapor pressure of a strictly horizontal water surface is attained (at the point O_4).

From the lowering of the vapor pressure, ZSIGMONDY and his pupils calculated the numerical value of the radius, R. On the assumption that the relations are those expressed in Fig. 107, the computation immediately gives the diameter of the capillaries, which is equal to $2R$. It was found that the capillary diameter for the silica gel is approximately 5 mμ.

From the observed vapor pressures ANDERSON[15] calculated the diameter of the pores for liquids other than water. His results are given below:

$2R$ for water	5.20 mμ
for alcohol	5.08 mμ
for benzene	5.58 mμ

This excellent agreement is a strong support for ZSIGMONDY's theory.[16]

Knowing that the capillaries in the silica gel have a diameter of about 5 mμ, we can compute the capillary rise from the formula:

$$h = \frac{2\sigma}{d_L R}.$$

For water, this amounts to several kilometers, which confirms our supposition as to the enormous force with which the water is sucked into the capillary pores.

The changes in Fig. 105 which result from the use of aged silica gels have been the subject of some interesting experiments.

Figure 108 indicates the sense in which these changes take place. The extreme limit is shown by the curve for hydrophane,

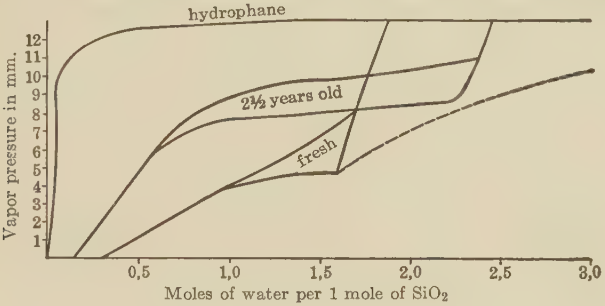

Fig. 108.

which is a form of silica that occurs in nature. It is apparent that the capillaries have slowly disappeared, and hence the curve for the oldest silica follows a course which almost coincides with the isobar for a level water surface. The reason for this is, no doubt, the instability of the colloidal structure. Röntgenographic research has shown that freshly prepared silica gel is hardly crystalline, but that as time goes on, there is gradually developed a regular orientation which is obviously due to the progressive arrangement of SiO_2 molecules into crystal lattices; hence, the capillaries and the concomitant phenomena disappear.

Nowadays the silica gel plays an important part as an adsorbent (Patrick). From the preceding discussion it is obvious that the dried silica gel has a large surface development, which is a prerequisite for an adsorbent. As a decoloring agent dried silica gel has lately found numerous applications.

88. The Gelatin Gel.—A gelatin gel differs from the silica gel discussed in the preceding section, by the absence of a final state corresponding to the point *O* in Fig. 105. This is due to the continued shrinkage of the walls of the gelatin gel while the water is being more and more completely removed. The silica gel at the point *O* has rigid walls, while the gelatin gel has supple walls. The cause of this elasticity is most probably the occurrence of water not only inside the capillaries but also in the walls of the pores. A distinction must be made, therefore, between the water of the walls (*cf.* Fig. 104) and the imbibed water which fills the pores. In computing, for the gelatin gel, the capillary diameter from the lowering of the vapor pressure, one does not find constant values but figures that decrease continually. Furthermore, different values are obtained, depending on the liquids dispersed in the gel. Nevertheless, there exists a relationship between the vapor-tension experiments on gelatin and those on silica gels, but in the former case the phenomenon is complicated by the pliability of the capillary walls.[17]

The continued deformation of the walls of the gelatin gel is closely connected with the well-known fact that many gels increase their total volume when they imbibe liquids. This phenomenon is called *swelling*.

89. Swelling.—When a dry gel is placed in a closed space and covered with a liquid, for instance, water, it may happen that the water is taken up with great intensity. A time-honored method of splitting the trunk of a tree consists in placing dry peas in a cavity of the trunk and then pouring water over them. The swelling peas split the wood with great force.

The process of swelling is, therefore, distinguished at once by two features: increase in volume, and pressure of swelling.

With regard to the former we must, however, qualify our statement. By an increase in volume is meant, generally speaking, the difference in *total* volume of all the participants before and after the process. The volume change that occurs when ammonium chloride is dissolved in water is not the difference between the volume of the solution and that of the water but the difference between the volume of the solution on one hand and the combined volumes of water and salt on the other; hence, the observation of the increase in volume of a gel immersed in water cannot be interpreted by saying that the process of swelling takes place with an increase in volume. The two things to be compared are the swollen gel and the dry gel *plus water*. This comparison leads to the inference that the process of swelling is characterized by a *decrease* in volume. This fact in itself is quite obvious: whatever the nature of swelling may be, at any rate, the fact remains that water is forced into capillary spaces and, as we have seen on page 15, increase in surface brings about compression of the dispersed phase.

Concerning the influence of pressure on the process of swelling, a clear distinction must be made: If gel and liquid are compressed *together*, an increase in pressure, according to the theorem of van't Hoff–Le Chatelier, will favor the process that involves a decrease in volume; hence, *uniform* pressure increases swelling. In general, however, we study something different: The pressure of the swelling gel is measured in such a way that the mobility of the water is maintained. We are then dealing with a *non-uniform* pressure, and, since the gel swells with increase of volume, this one-sided pressure will hinder the process of swelling.

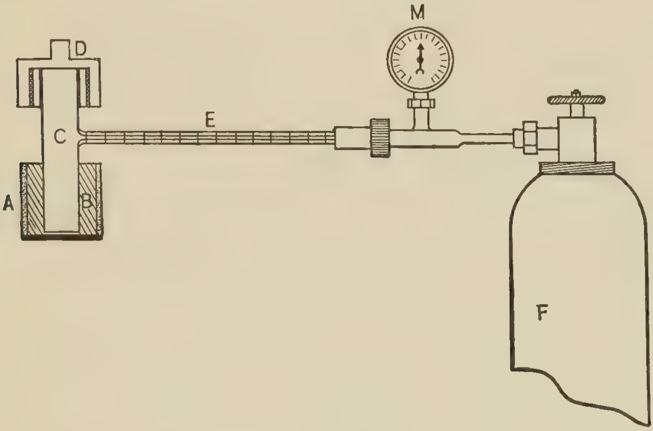

Fig. 109.

The latter is, indeed, an equilibrium process [18] in the sense that by exerting a non-uniform pressure on the swelling gel we can prevent further swelling. If the pressure applied is lower than the pressure of swelling under the given conditions, the swelling proceeds until both pressures are equal. If, on the other hand, the pressure exerted exceeds the pressure of swelling, water is squeezed out of the gel until the pressures are again the same.

It thus becomes apparent that small amounts of imbibed liquid correspond to large pressures of swelling and, conversely, that large quantities are taken up under small pressures of swelling. Posnjak [19] studied this relationship with the aid of an apparatus which is schematically represented in Fig. 109.

A porous pot, *A*, is attached to the glass tube, *C*, by means of the cement, *B*. The tube is closed by the cap, *D*, and connected to a graduated capillary, *E*, through which pressure can be exerted on the system in *C* by means of compressed gas in the cylinder, *F*. The gas pressure is read on the manometer, *M*.

Posnjak investigated, first of all, the swelling of raw Para rubber in different organic liquids. For this purpose he introduced a small disk of rubber through the tube, *C*, where it fell on the porous bottom. Mercury was poured into the tube until the latter was completely filled and the attached capillary partly filled. The porous pot was then placed in a beaker containing an organic liquid. The swelling of the rubber disk, caused by the liquid entering through the porous pot, was read by observing the displacement of the mercury in the capillary, *E*. Moreover, the gaseous pressure necessary to prevent the movement of the mercury could be readily determined, and in this way the pressures corresponding to different degrees of swelling were measured.

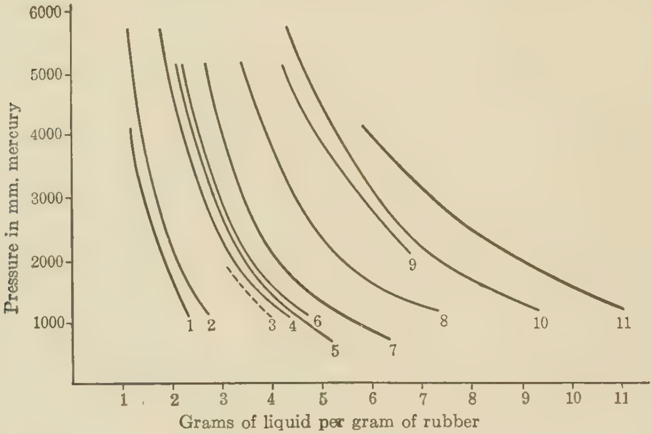

Fig. 110.

1. Ether
2. Ethylene chloride
3. Cumene
4. Cymene
5. Benzene
6. Toluene
7. Thiophene
8. Acetylene dichloride
9. Acetylene tetrachloride
10. Chloroform
11. Carbon tetrachloride

Posnjak's results are reproduced graphically in Fig. 110. The abscissae indicate the amounts of organic liquid taken up by the rubber, expressed by the ratio of grams of liquid taken up to grams of rubber. The ordinates represent the corresponding pressures of swelling in millimeters of mercury. The different curves relate to the liquids mentioned in the legend.

A careful examination of any of these curves confirms Posnjak's statement regarding the relation between the amount of absorbed liquid and the pressure of swelling. For ethylene chloride, for instance, the pressure reaches over 7 atmospheres when the rubber contains one and a half times its own weight of absorbed liquid. Posnjak could not extend his experiments to higher pressures because the porous pot was unable to withstand them. The general run of the curve shows clearly, however, the enormous pressure of swelling for the amount of liquid absorbed at the start.

Another thing which strikes us in examining Fig. 110 is the fact that the curves run practically parallel; hence, there is nothing specific about the behavior of these various organic liquids in the process of swelling. Freundlich points out that the following empirical equation applies:

$$P = P_1 c^k: \quad \text{or} \quad \log P = \log P_1 + k \log c,$$

where P is the pressure of swelling, c the concentration of the rubber in the swollen gel, P_1 the value of P for $c = 1$, and k a constant. The logarithmic curves are all straight lines running parallel to each other, since the value of the exponent k is the same for all. It appears also that k does not differ to any great extent for various gels. Whereas for rubber in a number of organic liquids k varies between the limits 2.5 and 3.3, Posnjak finds, for the system gelatin + water, the value 3.1.

The nature of the process of swelling has not yet been determined with certainty.[20] Nevertheless, the facts set forth in the preceding sections suggest that swelling is primarily caused by capillary suction in the gel (see p. 241). This pull can, as we have seen, amount to several kilometers of water pressure. For elastic gels such as gelatin, the inward suction causes a lateral pressure on the walls of the capillaries. The walls give way and at the same time take up liquid. The narrower the pores and the greater the capillary pressure, the more pronounced will be the pressure of swelling.

Katz [21] has made a Röntgenographic study of the change in the elementary cube in swelling threads. From his investigation the impression is gained that this unit remains unchanged, but that the constituents move further apart. This agrees well with the explanation given above.

The process of swelling has been studied more frequently under ordinary pressure than under a non-uniform pressure as applied by Posnjak.

A number of gels possess the property of swelling to a certain limit, the so-called maximum of swelling, while others swell continuously until the whole system is completely liquefied, as is the case with gum arabic. This maximum of swelling, then, appears to be the extreme limit to which the framework of the gel can be distorted, the limit depending, of course, on the temperature. A gelatin gel seems to show a tendency in this direction, but a careful investigation made by Arisz [22] showed that the swelling of gelatin as a function of the time cannot be expressed by a curve with a horizontal part, as sketched in Fig. 111, but follows the dotted line. It appears, therefore, that there is some tendency toward a maximum of swelling but that another process allows a show continuation of the swelling. We have to consider: (1) the capillary pressure of the water forcing its way into the intermicellar spaces and (2) the limit of elasticity of the gel structure, particularly at the hydrophobe spots (see Fig. 104). In case the latter is small, swelling leads to liquefaction (gum arabic); a greater value leads to an equilibrium (maximum of swelling) while for a large (but in the long run decreasing) value of the limit of elasticity, we obtain the kind of swelling that is characteristic of a gelatin gel (Fig. 111).

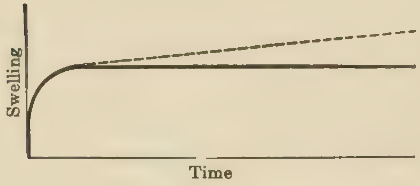

Fig. 111.

Most investigations on swelling have been performed by immersing plates of some substance, such as gelatin, in various liquids, and determining at definite intervals their increase in weight. Such experiments have been made by Hofmeister,[23] Wo. Ostwald,[24] and others.

The effect of aqueous solutions of electrolytes has been most extensively studied. Loeb[25] in recent years, performed a number of careful experiments on the influence of the hydrogen-ion concentration on the swelling of gelatin.

In dealing with these investigations we must, however, distinguish between two different methods of attack. Some of these workers studied the effect of an added acid by suspending a plate of glue, which is a gel of glue + pure water, in solutions of different concentration, while others first introduced acid into the gel and then allowed the gel to swell in water or solutions of acid.

Loeb applied the latter method and obtained results which are reproduced graphically in Fig. 112. We notice that a minimum of swelling occurs at the isoelectric point (see p. 210). Both increase and decrease of the hydrogen-ion concentration favors the swelling. Following the idea of Wilson, Loeb tried to explain this phenomenon on the basis of the Donnan equilibrium, by considering the gel contents as the liquid within an osmometer and the liquid in which the swelling occurs as the outside liquid. In this way he succeeded in obtaining a semi-quantitative agreement between theory and experimental results.

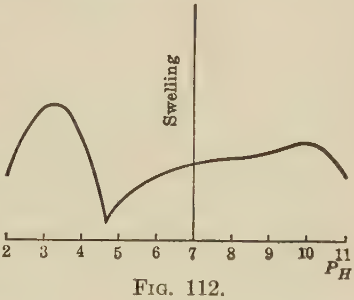

Fig. 112.

Hofmeister and Ostwald followed the first-mentioned method and recognized the comparatively complicated effect which neutral salts exert on the swelling. In general, it may be stated that the order in which salts influence the process of swelling is the one indicated by the *lyotropic series* of cations and anions; viz., if, for instance, the CNS ion greatly enhances the swelling, the SO ion will reduce it to a large extent. For this reason the lyotropic series is also called the Hofmeister series. Loeb considered the whole phenomenon as the result of the influence exerted by the salts on the hydrogen-ion concentration. Without denying this effect, the present writer wishes to emphasize the specific influence of this ionic series both here and elsewhere (see pp. 195 and 257). To his mind, a change in hydrogen-ion concentration cannot possibly explain the phenomenon.

90. Syneresis.—The converse of swelling is represented by a phenomenon which is usually called syneresis. It appears as a separation of water from the gel. When, for instance, a gelatin sol is allowed to gelatinize, a solid mass of gel is obtained, which on standing contracts and squeezes out liquid. The amount of aqueous liquid increases continually while the gel shrinks more and more. The phenomenon is also noticeable in the case of a swollen plate of gelatin where small droplets appear on the surface. In some cases of electrolyte-gelatinizing, syneresis is quite striking. When an electrolyte is added to a CeO_2 sol, the resulting gel forms a lump which fills the container completely. The gel soon contracts, and after a few days only a very small piece of gel is left in the surrounding aqueous liquid.[26] The same thing happens with a sample of gelatinized viscose.

In the last-mentioned case, what happens is probably this: Gelatinizing is, as was previously explained (*cf.* p. 231), the flocculation of strongly hydrated particles in the form of a coherent mass of gel. Flocculation, however, need not be complete, and this coagulation may only represent the first link in the chain of consecutive changes. FREUNDLICH and SCHUCHT,[27] as well as HAASE,[28] have shown that the size of the particles in flocculated suspensoids increases continuously. Apparently the same thing happens in the case of the CeO_2 sol. The water that is thus expelled from the pores of the gel represents the syneresis water. A similar progressive increase in the size of the particles may occur with the gel of agar-agar. Here, too, an expulsion of the water in the pores takes place, giving rise to the phenomenon of syneresis. Figure 104 (p. 234) demonstrates this clearly: In case there are several hydrophobe spots on one and the same particle, which is very likely to happen (for the sake of simplicity only *two* are shown for each particle) these will gradually tend to cohere, thus necessitating contraction of the gel and expulsion of the water in the pores.

91. Optical Properties of Gels.—In the preceding sections some reference has been made to optical properties of gels, insofar as transparency and TYNDALL effect were concerned (see pp. 230, 231). There is, however, one property which has been much studied and therefore deserves a separate discussion, viz., the double refraction that occurs under certain conditions.

It has been shown that the V_2O_5 sol exhibits the phenomenon of double refraction (see p. 143), which, however, is not noticeable as long as the location of the particles is haphazard. Orientation of the sol particles in parallel lines at once produces double refraction. This phenomenon, therefore, must be ascribed to " individual double refraction " of the constituent particles.

A piece of plate glass bent in one direction becomes double refractive. The same is true of fibrous alumina, which in itself does not consist of double-refracting particles but is composed of non-spherical constituents. These may become oriented in the same direction and thus give rise to double refraction. AMBRONN [29] found that this double refraction depends on the difference in refractive index of the particles and the surrounding medium. Hence, this so-called " double refraction of small rods " can be eliminated by choosing a medium that has the same index of refraction as the particles.

On examining the double refraction of gels, we note that unilateral deformation of a gelatin gel or of a celloidine gel causes double refraction. Either of the two above-mentioned types of double refraction is conceivable. It might be possible that bending produces lines of force along which rod-shaped particles orient themselves in the manner of the particles in the V_2O_5 sol. The second possibility is that the existing particles of the gel possess a double refraction of their own.

A remarkable study in this direction was made by AMBRONN.[30] A cube-shaped piece of cherry gum appeared to become double refractive when compressed, but this double refraction changed gradually with time, while the pressure remained the same. This points to a slow adaptation of the particles, and it may be inferred that both phenomena occur, viz., individual double refraction and double refraction caused by rod-shaped particles. When the pressure is released these two double refractions are restored successively.

An exhaustive study of WÄCHTLER [31] showed that both kinds of double refraction also play a rôle in gels of celloidine. This was proved by immersing the gels in liquids of gradually increasing refractive indices.

Röntgenographic investigations,[32] furthermore, have brought out the fact that many gels have a crystalline structure, so that the surmise of an individual double refraction is well founded.

It has been found, for instance, that rubber gives an X-ray spectrogram showing only the so-called amorphous rings. Stretch-ing of the rubber gel produces a characteristic diagram of lines and points such as is obtained with oriented crystallites.[33] Gelatin gels, likewise, exhibit this phenomenon.[34] It seems that the interference spetrograms produced by swelling gels are related to those obtained with gels oriented by tension.[35]

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PART IV

Special Cases

CHAPTER XVII

SPECIFIC COLLOIDS

92. Cases Intermediate between Suspensoids and Emulsoids.— Hitherto we have sharply distinguished between lyophile and lyophobe sols. It is obvious that in reality we often meet with cases which do not belong wholly to either of these two types. Nevertheless, we do well to make theoretical distinctions at first, and later to compare the more complicated reality with the extreme cases.

Heretofore we have assumed that the electric charge is a measure of the stability of suspensoids, while both charge and hydration are determining factors in the case of emulsoids. If this were so, the flocculation of a suspensoid sol would depend solely on the valence of the oppositely charged ion and not on its lyotropic position. The latter would exert its influence only on emulsoids. A careful examination of Table VIII (p. 70), which gives the flocculation values for the typical As_2S_3 sol, shows, however, that although the limiting values for different electrolytes are undoubtedly primarily dependent on the charge of the cations, there is unmistakable evidence of a slight lyotropic effect. In fact, the order of the flocculating values for a series of cations of the same valence is found to be:

$$Li > Na > K$$

and

$$Mg > Ca > Sr.$$

This lyotropic effect, which is barely evident in Table VIII, comes more strongly to the fore in the case of some other sols. In the following table are found the first flocculation values, i.e., the concentrations of electrolyte producing the first turbidity, for the sols of Mo_2O_5 and V_2O_5.[1] Although the effect of the valence of the cations can still be recognized (both sols are negatively charged), the enormous influence of the lyotropic series is quite manifest. Remembering that these sols give jelly-like precipitates, and further, that a sol of V_2O_5 readily sets to a gel which greatly resembles that of Al_2O_3, we are inclined to link this behavior with a possible hydration of these particles and thus establish a case intermediate between suspensoids and emulsoids. An argument in favor of this consideration is found in a recent investigation showing that the addition of alcohol to the sol strongly represses the effect of the lyotropic series on the flocculation value.[2] Hence, a removal of hydration reduces the lyotropic influence.

TABLE XXIX.

FIRST FLOCCULATION VALUES

Electrolyte	Mo_2O_5 sol	V_2O_5 sol
$\frac{1}{2}Li_2SO_4$	500	
LiCl	....	130
NaCl	60	50
KCl	12	17
RbCl	5	7.7
CsCl	2.6	
$Mg(NO_3)_2$	1.8	0.56
$CaCl_2$	0.77	0.25
$SrCl_2$	0.61	0.28
$BaCl_2$	0.19	0.23
$Ce(NO_3)_3$	0.22	0.013
$\frac{1}{2}Al_2(SO_4)_3$	0.14	0.005

The author does not believe, however, that this is an adequate solution of the problem. If it were merely a matter of dehydration, one would expect the strongly hydrated lithium ion to be a better flocculating agent than the slightly hydrated potassium ion, whereas the reverse is true. On page 196 the lyotropic effect was ascribed to two factors: viz., the hydration of the ions and the change in the molecular state of the water. Later investigations and recently proposed theories have connected the lyotropic influence with a third contributing factor. The water molecules influenced by the ion and forming, as one might say, the hydrated water of the ion, are probably oriented polarly in the manner depicted schematically in Fig. 113. A water molecule is here represented as a triangle with the hydrogen ion at one corner

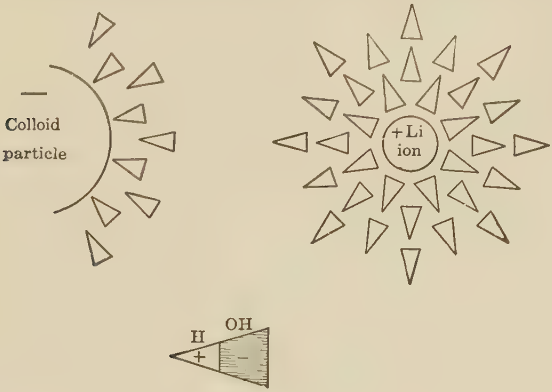

Fig. 113.

while the OH ion forms the base. A cation will fix the dipoles of water in such a way that the negative side of the water is turned toward the ion and the positive side away from it. The strongly hydrated lithium ion, therefore, causes a very pronounced orientation. A negatively charged colloidal particle likewise orients the surrounding water molecules, but in the opposite direction. The figure shows that the hydration of the readily adsorbed Li ion favors that of the negative particle; hence its hydration will be increased by the lithium ion and the critical potential at which flocculation takes place will be lower for LiCl than for KCl. Consequently, the highest flocculation value is for LiCl, the series being: Li > Na > K > Rb > Cs, instead of the other way round as would be the case if the salting out effect played any appreciable part.

Lyotropy, therefore, is probably not a hydration pure and simple, but one that orients the dipoles of water. This explains at once why, in the case of proteins, the lyotropic series are reversed when the charge of the protein changes from positive to negative.[3] Here, too, the similar or dissimilar location of the hydrated water determines the order of the lyotropic phenomena.

Another example, of the same type as the oxide sols referred to above, is the sulphur sol. Its flocculation values are presented in the following table. We notice again that, although the sol is negatively charged, a certain lyotropic effect, at least in the case of monovalent cations, is unmistakable.

However, not all sulphur sols belong to this type; on the one hand, we have sols prepared from sulphur dioxide and hydrogen sulphide or from thiosulphate and an acid; on the other hand, there are sols, made by dissolving sulphur in alcohol and pouring this alcoholic solution into water. The first-mentioned sols, which are all grouped under the term ODÉN's sols, show the behavior illustrated in Table XXX. The other kind, prepared according to the method of VON WEIMARN (see p. 166), possesses a normal suspensoid character. FREUNDLICH and SCHOLZ[4] found that the double layer in the case of ODÉN's sols consists of pentathionic acid (*cf.* p. 108). This acid enters into the reactions referred to, either as a by-product or as an intermediate compound. This thionic acid seems to be responsible for the peculiar character of the ODÉN sol, since it is closely related to the sulphur particle, owing to its sulphur content. It is also strongly hydrophile and therefore gives to the sol its pronounced hydration. The latter property has been definitely established by viscosity measurements.[5] Furthermore, the ODÉN sol is rich in amorphous sulphur, $S\mu$,[6] while the sol prepared according to the method of VON WEIMARN contains mainly crystalline sulphur, $S\lambda$. Following the

TABLE XXX

FLOCCULATION VALUE, ODÉN'S S SOL

Electrolyte	Flocculation value
$LiCl$	750
$NaCl$	190
KCl	85
$RbCl$	80
$CsCl$	95*
$MgCl_2$	1.5
$CaCl_2$	1.5
$BaCl_2$	1.5
$CeCl_3$	0.06

* It is not clear why the value for Cs is a little too high.

method of indicating the structure discussed on page 107, the Odén sol must be represented as follows: $\left|\overline{S\mu\ H_2O}\right|\ S_5O_6^{--}$.

Evidently, we have here again a connection between the hydration of the sol and the effect of the lyotropic series on the flocculation values. The sols hitherto discussed are, moreover, characterized by the fact that flocculation can occur more or less reversibly. The Odén sol shows this property to a great extent. The addition of an electrolyte to the sol produces flocculation, but a subsequent dilution with water is sufficient to dissolve the precipitate. Odén has made use of this property to purify his sols. Having found that the limiting value is a function of the size of the particles, he has been able to separate his sols in fractions of definite particle size by means of fractional precipitation.

The sols of Mo_2O_5 and V_2O_5 are likewise reversible in the sense that the coagulum obtained by centrifugal separation can be redissolved after one or more washings.[1] This renewed peptization is most readily performed in case the sol has been flocculated by a small excess of a monovalent cation with slight flocculating power. When precipitation has been brought about by a large excess of electrolyte or by a sudden addition of polyvalent cations, repeated peptization occurs only after prolonged treatment with water, and sometimes there is no peptization at all. The same is true of sulphur, where electrolytes that flocculate strongly hinder the re-formation of the sol.[5]

We naturally look for a connection between reversibility and hydration. The latter is, as we have seen, a stability factor but is not in itself sufficient to insure stability. A small electric charge is also necessary. Moreover, hydration interferes with the final destruction of primary particles, so that washing of the coagulum soon after precipitation raises the charge of those particles that have not yet coagulated, and in this manner a re-formation of the sol is made possible.

This whole phenomenon of repeptization again suggests the idea that the charge is not uniformly distributed over the surface of the particle (*cf.* p. 234), at least not directly after the addition of a flocculating electrolyte. In fact, it may be readily assumed that the flocculating particles adhere only on those spots which are discharged while other spots are still charged and exert a repelling action. Now an increase in these charges by a removal of electrolyte in the immediate neighborhood, viz., by washing with pure water, strengthens the repelling forces and the previous state of dispersion can be restored. This is, in general, always possible. Even the flocculation of an As_2S_3 sol or that of a gold sol is reversible for a few instants as can be seen when a sol, treated with an electrolyte solution, is diluted with the same sol (untreated) so that the final concentration is below the flocculation value. For a few moments, there are then *local* concentrations exceeding the flocculation value and in those spots the sol coagulates. Shaking the liquid restores the sol condition. If, however, we leave the coagulated As_2S_3 undisturbed for some time, the coagulation is permanent and hence not reversible. When sols of the type of V_2O_5 are used, the reversibility lasts a longer time since the hydration of these sols, likewise assumed to be localized in spots (see p. 234) acts in favor of a permanent stability.[6a]

The positively charged iron oxide sol, discussed on page 75, also shows unmistakable lyotropic phenomena. Table XI, page 74, indicates that the order of the flocculating monovalent ions is as follows: $I > NO_3$ and $Br > Cl$. Here, too, there is a reversibility resembling that previously considered, as found, years ago, by LINDER and PICTON.[7] Especially concentrated sols of ion oxide exhibit a marked reversibility. FREUNDLICH and ROSENTHAL [8] observed that a coagulated sol of iron oxide is returned to the sol condition by simply shaking the container; on standing, the sol again gelatinizes. This is the classical example of thixotropy, discussed in Sec. 85. It was found, furthermore, that this gelatinizing has the character of flocculation and hence may be considered as a reversible flocculation. The close connection of these flocculation phenomena with gelatinizing comes repeatedly to the fore in the discussion of the sols mentioned in this section.

93. Soaps.—Whereas in Sec. 92 we considered colloidal solutions combining the properties of suspensoids with those of emulsoids, we find that a soap solution is one combining the state of a true solution with that of a colloidal solution. By a soap solution we mean, in daily life, a solution with washing properties. We shall see presently that these properties are very noticeable in the alkali salts of the higher fatty acids. It is a remarkable thing that only those fatty acids which contain more than 12 carbon atoms in their molecule yield solutions that exhibit the peculiar properties of capillary [9] and electrical [10] nature which are connected with common soap solutions. Of the salts referred to, the sodium and potassium salts of oleic acid, stearic acid, and palmitic acid are the ones that have been most frequently studied.

In alcoholic solutions, soaps behave like substances in true solution.[11] The aqueous solution acts in such an extraordinary manner that the older investigations give a rather confusing idea regarding the structure of these systems. Modern researches, particularly the excellent experiments performed by McBain,[12] have considerably broadened our knowledge in this field.

If we study the structure of a soap solution by measuring the elevation of the boiling point (the method of the dewpoint determination has been found to give the best results), we can compute the mol number, i, according to the formula of van't Hoff. The value of i for soap solutions appears to be less than unity. At first view, one might infer that electrolytic dissociation is, therefore, out of the question, since where this occurs i is of course more than unity. This conclusion, however, does not agree with the fact that a soap solution conducts the electric current exceedingly well.

It has, for a long time, been customary to ascribe these peculiar properties of soap solutions to hydrolysis. The hydrolytically separated fatty acid or acid salt of fatty acid would then be osmotically inactive, and only the alkali formed by hydrolysis would be responsible for the rise in boiling point and the electrical conductance. McBain's researches showed, however, that the concentration of the free OH ions in these solutions is comparatively small. Disregarding the possibility that hydroxyl ions are adsorbed,[13] we must conclude from this fact that hydrolysis plays an insignificant rôle in the soap solution.

The results of the determinations of dewpoint and conductivity can only be reconciled by the assumption that we have simultaneously electrolytic dissociation and colloid formation. A value of i in the neighborhood of unity results from the compensation of these two factors. It is quite obvious that part of the soap is in true solution. The more dilute the solution, the greater the percentage of soap in true solution. The only question is: In what form is the colloidal constitutent present in the soap solution?

McBain thinks that this colloid exists in two forms: one part, which he calls *neutral colloid*, consisting of undissociated soap molecules; and another part, peculiar to soap solutions, viz., *ionic micells.* These are presumably aggregates of acid anions forming one polyvalent anion in equilibrium with a corresponding number of free alkali ions. The osmotic properties of the solution are then wholly due to the slight quantity of soap in true solution and to the alkali ions of the ionic micells. The remaining constituents are practically inactive osmotically.

It appears to the writer that this dualistic representation is superfluous. The collodial constituent can be considered wholly in accordance with the ideas previously developed in connection with protein systems (see p. 207). A colloidal soap particle consists probably of a nucleus of salt molecules, only those on the outside being ionized and taking part in the formation of the electric double layer. Furthermore, these particles no doubt contain the small amount of free fatty acid due to the slight hydrolysis.

The diffuse outer coating of the double layer contributes to the osmotic effect, as was also previously indicated on page 223. All the data obtained by McBain can be readily explained on the basis of this simple conception. Miss Laing[14] has carried out electrical transference measurements on soaps, which are in complete accord with those of Varga and Wintgen, discussed in detail on page 112.

The colloidal constituent of soap solutions may be represented by:

$$\boxed{\begin{matrix} NaX \\ HX \end{matrix} \quad H_2O} \; X^-,$$

where X stands for the fatty acid radical. Hence, we have in a soap solution the following participants:

$$NaX \quad Na^+ + X^- \quad Na^+ + OH^- \; \boxed{\begin{matrix} NaX \\ HX \end{matrix} \quad H_2O} \; X^- + Na^+ \text{ (or } H^+).$$

Another peculiarity of soap systems is the behavior of solidified sols. The investigations of McBain[15] have shown that there are two things to be considered here, viz., the setting to the state of *gel* and the formation of a *curd*, a gel being transparent while a curd is opaque. One and the same sol under certain conditions sets to a gel, and under other conditions solidifies to a curd. For instance, a sol of 0.6N sodium oleate, when slowly cooled between 25° and 6°, forms a transparent gel which on prolonged standing (e.g., after two days) changes into a curdy mass. Immediate cooling below 6° produces a curd at once. The change from sol to gel occurs, strange to say, without any alteration of conductivity, whereas the formation of a curd takes place with increase of conductance. Ultramicroscopically, both sol and gel are void, while the curd contains long threads or needles. Evidently the gel is composed of hydrated micells which occupy haphazard positions, while the curd particles arrange themselves in the form of elongated crystals in the same manner as the particles of an aged V_2O_5 sol. In fact, the intermicellar liquid of a curd is in reality a saturated true solution, and curd formation is, therefore, simply crystallization from a supersaturated solution. This is, furthermore, in line with the fact that the solubility of soaps decreases strongly when the temperature is lowered.

The cleansing action of soaps has, in the past, been ascribed most frequently to the hydrolytically separated alkali. CHEVREUL explained the soap action as a separation of the fats under the influence of the free alkali, but this concept is entirely inadequate and could never account for the removal of substances other than fats. In later years, especially since the work of SPRING,[16] the cleansing is explained by assuming that any dirt that may be present is emulsified by capillary action of the soap and thus transferred from the object to be cleansed to the soap solution. In the light of the boundary theories discussed on pages 41, 96, and 207, this line of reasoning is quite plausible.

94. Emulsions.—By emulsions we usually mean systems in which one liquid is dispersed in another. In recent years these systems have attracted a great deal of attention, and CLAYTON [17] has written a very readable résumé on emulsions. Technically they are also of great importance.[18]

We possess a fairly good knowledge of systems in which oil is finely dispersed in water. Generally speaking, such a system is unstable unless the oil is present in small concentration only. In this case, according to the theory of VON SMOLUCHOWSKI (*cf.* p. 117), the oil particles coalesce very slowly. We have met such emulsions repeatedly in preceding chapters (*cf.* pp. 60, 68 and 85). It may be remembered that the investigations of DONNAN,[19] ELLIS,[20] POWIS,[21] and others have shown these (always very dilute) oil-in-water emulsions to be suspensoid in character, since their stability is governed exclusively by the electric charge. The mechanism of these systems is, therefore, fairly well known to us.

More concentrated emulsions cannot be obtained by merely shaking the constituents. In order to obtain a stable emulsion, it is necessary to add a stabilizing agent, which, for obvious reasons, is often called an *emulsifier*. Alkali soaps are particularly well adapted for this purpose.

On the other hand, there are emulsions of a totally different type: Instead of dispersing oil, as dispersed phase, in water as dispersion medium, we are able to do the reverse, viz., disperse water in oil. In this case the water is present in droplets distributed in a continuous oil phase. The word " oil " is used here in a general sense, indicating any organic liquid that does not mix freely with water.

It is of prime importance to know how a water-in-oil system may be distinguished from an oil-in-water system. Fig. 114 represents both systems schematically, the shaded portion indicating the oil phase. One method consists in adding a few grains of a dye, soluble in oil but not in water, for instance, sudan III. An oil-in-water system is not colored because the dye cannot reach the oil, whereas a water-in-oil system readily takes on the color of the dye.

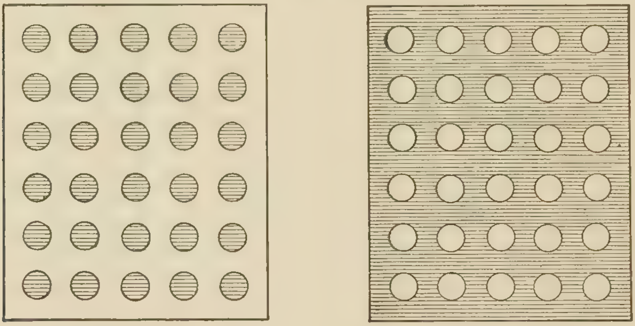
Oil in Water Water in Oil

FIG. 114.

Another way is the following: A drop of the emulsion is placed on a glass slide next to a drop of water. When contact is established between the two drops there will be coalescence in case we are dealing with an oil-in-water system; conversely, a water-in-oil system will coalesce with oil but not with water. The microscope readily reveals the difference.

A third method is furnished by the measurement of the electrical conductance. Whenever water is the dispersion medium the conductivity will be fairly good on account of the presence of electrolytes in the water. With oil as dispersing phase the conductance will be extremely small.

In the early days it was thought that it was entirely a matter of the ratio between the constituent phases, whether an oil-in-water or a water-in-oil emulsion was obtained. Suppose that all the drops of the emulsion just touch each other. Then we know, from the theory of piled spherical balls, that at most only 74 per cent of the total volume can be occupied by the spheres, provided they are all of the same size and are incompressible. Wa. Ostwald [22] first postulated that both emulsions would be capable of existence, depending on whether the ratio of the two phases is above or below 0.74. Pickering,[23] however, showed experimentally that this hypothesis was untenable, since he could make emulsions in which the dispersion medium occupied only 1 per cent of the total volume. Evidently the drops are then compressed so that the dispersing phase forms only thin films between them. Later investigations have made it clear that the amount of the phase plays a subordinate part, while the determining factor which governs the type of emulsion is the added emulsifier. Experiments of Clowes [24] and Bhatnagar [25] have shown that, in general, alkali soaps produce oil-in-water systems, while the soaps of the alkaline earth metals, Fe, Al, and Zn, favor the formation of water-in-oil emulsions. For example, if a system consisting of equal volumes of water and oil is stabilized by means of a sodium soap, the first effect of adding barium chloride is to destroy the stability. When the amounts of sodium soap and barium chloride have become equivalent and a barium soap has been produced, the system is extremely labile. The addition of more than an equivalent quantity of barium chloride reverses the system and a water-in-oil emulsion is formed.

These water-in-oil systems are (in fairly concentrated solutions), as a rule, very viscous or, to express it more correctly, plastic. They form paste-like masses, somewhat in the nature of butter or margarin.

Now, in order to find out what is the determining factor which makes an emulsifier form either an oil-in-water or a water-in-oil emulsion we must know, first of all, *how* an emulsifier exerts its emulsifying action.

This question might be answered by a direct application of the theory of Langmuir and Harkins. In fact, the pronounced heteropolar character, the strong capillary-activity and the vigorous emulsifying action of soaps immediately suggest a solution in this direction. As a matter of fact, a theory of emulsification along these lines has been worked out by Hildebrand [25] and his co-workers. Apart from certain inherent contradictions in the methods of testing this theory, one is inclined to be sceptical towards this trend of thought since substances without pronounced polar character, such as resins, and even a strongly apolar substance, like charcoal (soot) emulsify as well as soaps do. Hence, neither heteropolarity nor spreading in monomolecular layers can play a rôle. Charcoal, for instance, does not dissolve either in in water or in oil and must, therefore, exert its emulsifying action heterogeneously.

We might ask ourselves: Is, perhaps, a typical emulsifier a heterogeneous constituent of the emulsion? There is every reason to answer this query in the affirmative. Although it is true that Holmes and Williams [27] found a few typical heteropolar substances that dissolve either in the water—or in the oil phase (alcohols, fatty acids), nevertheless these compounds are not genuine, vigorous emulsifiers. The emulsions thus obtained retain a typical suspensoid character and their stability depends largely on the electric charge of the particles whereas this is not the case with the true, stable emulsions emulsified by heterogeneous admixtures. In this class we must place the soaps in spite of the fact that soaps dissolve in molecular dispersion in water at higher temperatures because they are less suitable as emulsifiers the better they dissolve in water. All good emulsifiers are microheterogeneous, or colloidally dispersed, and their emulsifying action is apparently dependent on their heterogeneity since they accumulate in the boundary of the emulsified particles. This fact can be readily observed under the microscope in emulsions stabilized by soot.

For a long time a connection has been sought between the emulsifying power of an emulsifier and its capacity to wet the water—or (and) the oil phase. The following figures [28] (115–118) will show to what extent the wetting power determines the emulsification.

In the figures one liquid—let us say water—is indicated by broken lines while the second one (the oil phase) is represented by the dotted area and the emulsifier by double cross-hatching. Assuming that the emulsifier is wetted to a greater extent by the

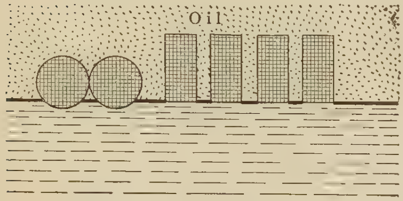

Fig. 115.

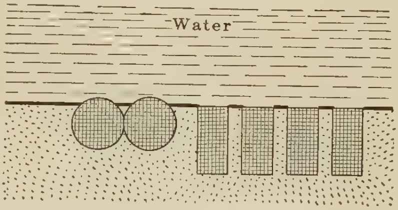

Fig. 116.

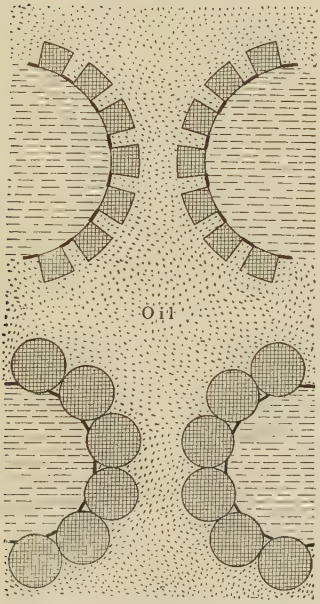

Fig. 117.

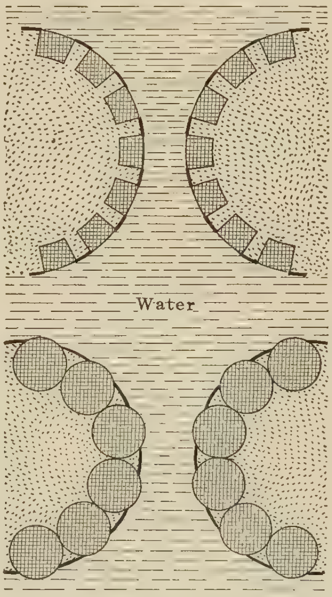

Fig. 118.

oil than by the water, we find that the emulsifying particles remain on the oil side of the oil-water interface, a condition which is schematically shown in Figs. 115 and 116. Figure 116 is the same as Fig. 115, only upside down in order to bring out more clearly the difference between Fig. 117 and Fig. 118 underneath.

What will happen now, when the two phases emulsify? Figure 117 shows water drops in oil and Fig. 118 oil drops in water. The greater wettability by oil is expressed in these figures by the location of the emulsifying particles on the oil side of the interface. It is at once obvious that the emulsion in Fig. 117 is stable and that in Fig. 118 unstable. In the latter case the collisions resulting from the Brownian movement greatly increase the probability of oil coming in contact with oil, thereby causing the drops to coalesce. The enlarged drops show the same type as before and on colliding with other drops again coalesce, in other words, the emulsion *breaks.* The condition sketched in Fig. 117 excludes the probability of water coming in contact with water since the emulsifying particles prevent this. Hence, an emulsifier which is more readily wetted by oil than by water, is a stabilizer for the system water-in-oil and, conversely, an emulsifier that is wetted to a greater extent by water than by oil, stabilizes oil-in-water systems.

As a matter of fact, alkali soaps are wetted more readily by water and soaps of alkaline earths are wetted more readily by organic liquids. Investigations of BARTELL [29] carried out with a very ingenious apparatus have considerably extended our knowledge of wettability. Charcoal is wetted much less by water than by organic liquids and accordingly emulsifies water in oil. Silica, on the other hand is wetted much better by water than by oil. Hence sand emulsifies oil in water.

Another important problem is: How are emulsions formed? There are two requisite conditions to be fulfilled: (1) one of the liquids must be finely divided; and (2) the droplets formed must be sufficiently stabilized to keep them from coalescing. The first part of this problem plays, in general, no rôle in the discussion of suspensoids, since the existence of discrete primary particles is an essential prerequisite and the preparation of suspensoids, insofar as it necessitates a dispersion method (*cf.* p. 166), merely involves a peptization process. In the case of emulsions the subdivision of the previously continuous phase may be brought about by such minute mechanical force that a second factor must be taken into consideration in the preparation. One of the liquids or both are finely divided in the presence of an emulsifier by mechanical means (shaking; or squeezing one liquid through narrow pores into the other liquid as is done in homogenizers). On shaking, one obviously divides both liquids, one into the other so that there are formed, simultaneously, both oil-in-water and water-in-oil systems (frequently, very complex water-in-oil systems in oil-in-water systems) but Figs. 117 and 118 have demonstrated that the emulsifier stabilizes only one type of emulsion the other being readily destroyed. We, therefore, readily understand why frequent shaking with intermittent partial separation in layers, is necessary for perfect emulsification.

It is thus seen that an entirely new factor enters into the stabilization of emulsions, a quantity which is really of a mechanical nature, depending on the capillary properties (wettability) of both liquids and of the emulsifier. In addition to this factor we have to consider the well-known quantities of charge and hydration. However, the mechanical factor alone is capable of stabilizing emulsions in a number of cases.

95. Flocculation by Several Electrolytes.—The limiting values for a single electrolyte were discussed at length in Chapter IV. In order not to interrupt the course of the argument, the author omitted the complication which is introduced by the simultaneous addition of several electrolytes. This matter has been much studied in recent years,[30] mostly with the intention of obtaining a better insight into the peculiar antagonistic action which some cations exert on each other physiologically. Whether the study of flocculation values can really settle this point is a debatable question; hence, the matter will be discussed exclusively from the colloid-chemical point of view. If the flocculation value of a given sol amounts to 100 millimoles per liter, with potassium chloride as a precipitating agent, the total concentration of a mixture of potassium chloride and sodium chloride will likewise attain the value of 100 millimoles at the limiting concentration. In case the flocculating ions are not as closely related as the potassium and sodium ion, the limiting value for the mixture cannot be computed additively. It is quite remarkable to note that the addition of a second salt does not lower the flocculation value of the other salt, but, on the contrary, raises it. Representing the flocculating values of each of the salts, used separately, by 100, we notice, from the data given in Table XXXI, that the limiting values of mixtures often exceed 100. The two salts, therefore, do not cooperate, but, in a way, interfere with each other's flocculating activities. Whereas the As_2S_3 sol is flocculated by 0.8 milli-

TABLE XXXI [31]

As_2S_3 sol		HgS sol		HgS sol	
LiCl	$MgCl_2$	$\frac{K_4Fe(CN)_6}{4}$	$MgCl_2$	$\frac{K_3Fe(CN)_6}{3}$	$MgCl_2$
0	100	0	100	0	100
25	138	12.5	180	33	130
50	156	20	190	66	60
72	180	25	200	100	0
100	0	44	230		
		62	60		
		100	0		

HgS sol		HgS sol		Se sol	
$\frac{K_2SO_4}{2}$	$MgCl_2$	KCl	$MgCl_2$	$\frac{K_4Fe(CN)_6}{4}$	$MgCl_2$
0	100	0	100	0	100
16	110	16	110	8	112
33	120	33	120	16	116
100	0	100	0	25	122
				33	122
				50	100
				100	0

mole of $MgCl_2$ per liter (= 100 in the table), 1.25 millimoles of $MgCl_2$ (corresponding to the comparative value 156) will be required after the previous addition of half the flocculation value for LiCl.

From the examples quoted in Table XXXI it appears, therefore, that whenever lithium chloride is first added considerably more than the amount demanded by the rule of mixtures is necessary to discharge the sol to its critical potential. This justifies the surmise that the addition of the first salt has raised the potential. As a matter of fact, we met, on page 85, with cases where the boundary potential was increased by salt addition. The same is evidently true for the salts mentioned in Table XXXI. Special investigations on cataphoresis of these sols have confirmed this assumption.[31] Another point which strikes us in looking over the figures in the table is that ions that greatly increase the charge are highly suitable for raising negative charges, as, for instance, SO_4^{--} and $Fe(CN)_6^{----}$.

The problem of flocculation by means of mixtures of electrolytes is, therefore, reduced to the following: Whenever a salt raises the charge, its addition will also raise the flocculation value of a second salt. This leads to another question: Why does the first salt raise the charge? This matter has been previously discussed. One is inclined to say that in such a case the anions are adsorbed more strongly than the cations. The chlorine ion, for instance, might be adsorbed more strongly than the potassium ion, and even to a greater extent than the lithium ion, which in turn suggests a connection with the lyotropic series. Since it is difficult, in cases where displacement adsorption plays a prominent part, to secure experimental evidence on the manner of adsorption, we must, for the present, confine ourselves to the statement of the interrelation of elevation in charge and increase of limiting value.

96. Photo-colloid Chemistry.—Comparatively little is known with regard to the effect of light and other radiations on colloidal systems. Mention should be made of the work of FERNAU and PAULI [32] on the effect of β- and γ-rays on the sol of CeO_2 and of an investigation by FREUNDLICH and NATHANSON [33] on the influence of light on the As_2S_3 sol.

We are, of course, better acquainted with the influence of light on the photographic plate.[34] The so-called photographic emulsion (the word emulsion naturally has a different meaning here from the one given to it in Sec. 94 of this chapter) consists of a silver halide dispersed in a gelatin gel. Any kind of silver halide may be employed, such as AgCl in diapositives or AgBr and AgI mixtures in plates and films. One may prepare these emulsions by pouring into the same container dilute solutions of silver nitrate and alkali halide in the presence of gelatin, and allowing the whole to set. Colloidal silver halide is formed, but in such a high state of dispersion that the reactivity of the emulsion is exceedingly slow. In order to produce rapid plates, a process of ripening is applied whereby small grains grow to larger ones. We are, as yet, not certain whether this grain growth is the cause of the rapid action, or an incidental side reaction. The grain growth is essentially a recrystallization process.

The exposure of the photographic plate to light results in the formation of the so-called latent image and corresponds to a reduction of the silver halide particles. For a long time it has been doubtful whether there occurs a reduction to a subhalide or to metallic silver. Modern investigations, however, have shown that the exposed plate contains silver halide grains in which minute nuclei of silver are produced. When the plate is developed, only those silver halide particles are reduced to silver that already contain a tiny silver nucleus in the latent image. The researches of SVEDBERG [35] have brought out that the course of the process is really as follows: One silver nucleus in a grain of silver bromide makes the whole grain suitable for subsequent developing, whereas a grain without a nucleus remains unchanged unless it is in close contact with another grain containing such a center.[36] The exposed plate represents, therefore, a peculiarly complicated colloidal system, viz., a gelatin gel with dispersed silver bromide grains, part of the latter containing one or more silver nuclei.

In recent years a new question has cropped up: By what mechanism does the light produce the silver nuclei? While in the past the action of the incident light was measured by the degree of blackening of the plate, we have been enabled in recent years, by using plates with a single layer of silver halide grains, to count the number of grains attacked by a definite quantity of radiation. SVEDBERG [37] found that by using α-rays (i.e., charged helium atoms) each grain hit by an α-particle is made fit for subsequent development. With β-rays or ordinary light, as a source of radiation, we do not know whether each quantum of light plays the same part as an α-particle. On the contrary, various investigators have pointed out that no confirmation of the theory of light quanta can be looked for in this direction. Some experiments of CLARK [38] have even indicated that a solution of sodium arsenite exerts exactly the same effect as light.

Consequently, there is, as yet, nothing certain about the mechanism of the separation of the silver nucleus from the silver halide. What interests us in particular is why certain parts of the grain are better adapted for nucleus formation than other parts. The impression is gained that specific points in the photographic emulsion are favored because of the presence at those spots of catalysts which pave the way for the appearance of the silver nuclei of the latent image. Recently, SHEPPARD [39] showed that gelatin actually contains decomposition products which highly favor the sensitiveness of the emulsion. It is probable that these catalysts are located at certain points of the grain and that herein lies the explanation of the local predisposition of the grain. The problem of the photographic emulsion is, however, in its first stage, and the fact that we are dealing with a rather complicated system of dispersed particles means that colloid chemistry will without doubt be called upon to furnish the clue to the solution.

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AUTHOR INDEX

A
Abramson, 237, 252
Adam, 44, 50
Adams, 252
Alexander, 81, 117, 160, 172, 174
Ambronn, 144, 251, 253
Anderson, 242, 252
Arisz, 217, 218, 248, 252
Arkel, A. E. van, 63, 81, 121, 122, 123, 128, 142, 145
Arkel-Adriani, Mrs. H. G. van, 95
Arrhenius, 3, 50, 170
Aquino, d'-, 203
Avogadro, 141, 149

B
Bachmann, 160, 230, 231, 236, 239, 252
Bakhuis-Roozeboom (see Roozeboom)
Bancelin, 180, 188
Bancroft, 173, 174, 275, 276
Bartell, 41, 49, 50, 228, 252, 270, 276
Barus, 170, 175
Bary, 174
Beans, 87, 95
Bechhold, 50, 158, 160
Beckenrath, von, 116
Bemmelen, van, 40, 50, 80, 170, 175, 237, 238, 239, 240, 252
Bendien, 95
Benson, 18, 49
Berenyi, 49
Bergmann, 188, 189
Bhatnagar, 267, 276
Billitzer, 80, 175
Biltz, 136, 143, 146, 159, 160, 224, 227
Bingham, 189
Bishop, 160
Bjercke, 50
Bjerrum, 160
Boer, de, 29, 49
Bogue, 174
Boltzmann, 98
Bose, 145, 146
Boyle, 44
Bragg, H. L., 133, 145
Bragg, Sir W. H., 109, 133, 145
Bredig, 116, 167, 168, 171, 175
Briggs, 58, 63, 80, 88, 95, 204
Brinkman, 49
Brossa, 92, 95
Brown, F. E., 50
Brown, R., 147, 148, 160
Browne, 79, 81
Bruyn, Lobry de, 129, 145, 172, 175
Bützchli, 240
Bungenberg de Jong (see Jong)
Burton, 60, 62, 63, 67, 68, 80, 153, 160, 172, 174, 175, 185

C
Cassius, 94
Chatelan, 49
Chevreul, 265
Clark, 274, 276
Clayton, 265, 275
Cleveland, 174
Clowes, 267, 275
Coehn, 104, 116, 171, 175
Cotton, 140, 145
Couette, 182, 189
Cremer, 115, 160
Currie, 62, 63

D
Dallwitz, von, 49
Dam, van, 49

d'Aquino (see Aquino)
Davies, 50
Debye, 3, 8, 84, 85, 95, 109, 134, 135, 144, 145, 188
de Boer (see Boer)
de Haas-Lorentz (see Haas-Lorentz)
de Jong (see Jong)
Desaga, 156
Devaux, 42, 43
Dhar, 276
Diesselhorst, 143, 146
Doerinckel, 81
Donnan, 49, 155, 173, 219, 221, 222, 223, 224, 227, 249, 265, 275
Dorn, 52, 53, 62
Draper, 276
DuClaux, 109, 112, 116, 173, 175, 224, 225, 227
Duin, van, 41, 50
du Nouy (see Nouy)
Dunstan, 203

E

Eastlack, 87, 95
Ehrlich, 140
Einstein, 149, 150, 151, 160, 180, 181, 182, 183, 184, 185, 188
Elissafoff, von, 54, 55, 56, 63, 80, 103, 115
Ellis, 63, 87, 171, 173, 175, 265, 275
Elster, 146
Ettisch, 77, 81, 95
Exner, 160

F

Fajans, 111, 116
Fanselow, 218
Faraday, 172, 175
Fernau, 252, 273, 276
Fick, 150
Finckle, 276
Findlay, 218
Franz, 87, 105, 116
Freundlich, 23, 24, 30, 49, 50, 63, 71, 72, 73, 76, 77, 80, 81, 88, 92, 95, 98, 99, 101, 103, 108, 115, 116, 127, 128, 143, 146, 160, 172, 173, 174, 175, 216, 236, 237, 247, 250, 252, 253, 260, 262, 273, 275, 276
Frey, 253
Friedemann, 95
Frieden, 87, 95
Frumkin, 52, 63, 116
Fuchs, 109, 116
Fürth, 95, 160

G

Galecki, von, 123, 128
Gann, 81, 95, 128, 252
Geitel, 146
Gerngross, 253
Ghosh, 276
Gibbs, 18, 19, 20, 49
Goethe, 130
Gortner, 214, 218
Gosh, 276
Gouy, 98, 100, 115, 160, 174, 203
Graetz, 63, 115, 174
Graham, 6, 8, 87, 95, 156, 169, 170, 175
Griffin, 45
Grinten, van der, 63
Gyemant, 98, 115

H

Haase, 250, 253
Haas-Lorentz, Mrs. G. L. de, 160
Haber, 98, 99, 115
Hahn, von, 145
Hardy, 67, 68, 69, 71, 80, 88, 171, 172, 175, 184, 189, 268
Harkins, 41, 45, 46, 48, 49, 50, 52, 103, 106, 200
Hatfield, 173
Hatschek, 174, 175
Hedges, 153, 160
Heinz, 87, 105
Helmholtz, von, 62, 96, 97, 101, 102, 115, 174
Henkeler, 50
Herzog, 188, 189, 253
Hess, 182, 189, 253
Heyer, 157, 160
Hildebrand, 268, 276
Hittorf, 3, 114
Hoeber, 275
Hoff, van't, 3, 36, 154, 155, 156, 219, 221, 222, 223, 245, 263

Hoffmann, 214, 218
Hofmeister, 248, 249, 252
Holmes, 174, 268, 276
Horovitz, 115
Hückel, 3, 30, 49, 84
Hull, 145
Hulshof, 49

I

Iliin, 29, 49
Ishizaka, 128

J

Jaeger, 49
Janke, 188, 189
Joachimsohn, 77, 81
Johnston, 252
Jong, H. G. Bungenberg de, 188, 189, 200, 203, 204, 234, 235, 252
Jordis, 173, 175

K

Katz, 189, 252, 253
Kjeldahl, 185
Klemensiewicz, 98, 99, 115
Knehe, 189
Koch, 50
Kohlrausch, 3, 112
Kohnstamm, 49
Kolthoff, 50
Kraemer, 160, 218
Krafft, 275
Krause, 253
Kruyt, 41, 50, 57, 63, 79, 80, 81, 87, 88, 95, 98, 99, 111, 115, 116, 121, 122, 123, 126, 128, 146, 173, 189, 203, 211, 218, 252, 253, 275, 276.
Kühn, 145, 174
Kugelmass, 174

L

Labes, 57, 63
Lachs, 50
Laing, 264, 275
Lange, 275
Langmuir, 27, 29, 38, 41, 42, 43, 44, 49, 50, 52, 103, 106, 200
Laplace, 13
Laue, von, 109
Le Chatelier, 36, 245
Lecompte du Nouy (see Nouy)
Lenard, 49
Leonhardt, 146, 275
Lier, 203, 218
Liesegang, 168
Lillie, 224, 228
Linder, 9, 67, 79, 80, 170, 172, 175, 262, 275
Lobry de Bruyn (see Bruyn)
Loeb, F., 160
Loeb, J., 203, 208, 210, 211, 212, 213‘ 223, 224, 226, 227, 228, 249, 252
Losev, 50
Lottermoser, 116, 128
Lüppo-Cramer, 276

M

Made, Miss J. M. van der, 50, 252
Majorana, 146
Manegold, 160
Marc, 34, 49, 50, 163, 168
Marcelin, 45
Marck, 107, 116
Matsuno, 75, 81
Matthews, 79, 81
Maxwell, 69, 127
McBain, 263, 264, 275
McLewis, W. C., 25, 26, 49
Mecklenburg, 104, 116
Michaelis, 41, 50
Mie, 130, 131, 145
Millard, 204
Miller, 40, 41, 49, 50
Minne, van der, 276
Moore, 228
Morawitz, 73, 80, 81
Mouton, 140, 145
Müller, 122, 123, 128
Mukherjee, 111, 116, 173, 276

N

Nägeli, von, 109, 116, 170, 175
Nathanson, 273, 276
Neidle, 160
Neisser, 95
Nernst, 51, 99, 103, 225, 226

Neubert, 253
Neumann, 50
Nichols, 143, 146
Nouy, Lecompte du, 49

O

Ober, 76, 81
Odén, 145, 260, 261, 275
Ohm, 83
Osterhof, 276
Ostwald, Wa., 267, 275
Ostwald, Wi., 3, 172, 175, 181, 191
Ostwald, Wo., 7, 50, 145, 160, 173, 174, 175, 184, 189, 204, 248, 249, 252

P

Paneth, 116
Patrick, 25, 26, 49, 243
Pauli, 109, 116, 160, 203, 208, 209, 224, 252, 273, 275, 276
Pennycuick, 109, 116
Perlak, 116
Perrin, 55, 57, 63, 149, 150, 151, 152, 153, 160, 172, 175
Pickering, 267, 275
Picton, 9, 67, 79, 80, 170, 172, 175, 262, 275
Pockels, 50
Poiseuille, 84, 181, 182, 232
Polanyi, 29, 49
Porter, 153, 160
Posnjack, 245, 246, 247, 248, 252
Posternack, 275
Postma, 252
Potts, 275
Powis, 60, 63, 68, 69, 80, 85, 87, 88, 95, 98, 99, 115, 128, 173, 265, 275
Pringsheim, 188, 189
Proctor, 223, 227

R

Raoult, 3
Raydt, 116
Rayleigh, 42, 130, 145
Reinboldt, 160
Reinders, 95, 144, 146
Reitstötter, 121, 128, 168
Richards, 49
Righter, 276
Rinde, 227
Roaf, 224, 228
Robinson, 203, 275
Rona, 41, 50, 98, 99
Roozeboom, Bakhuis, 252
Rosenthal, 262, 275
Rothlin, 189

S

Salmon, 275
Samec, 208
Scarpa, 193, 203
Scheerer, 170, 175
Scherrer, 8, 109, 134, 135, 144, 145, 188
Schiller, 115
Schleicher, 156
Schmidt, 38, 50
Schneider, 170, 175
Scholz, 95, 108, 116, 260, 275, 276
Schreinemakers, 227, 228
Schröder, von, 217, 218
Schucht, 73, 81, 95, 250, 253
Schüll, 156
Schulze, 71, 170, 172, 175
Schuster, 146
Selmi, 169
Sen, 276
Sheppard, 275, 276
Siedentopf, 135, 144, 145, 146
Sims, 252
Smith, Alex, 275
Smith, C. R., 217, 218
Smoluchowski, von, 63, 96, 115, 117, 119, 120, 121, 123, 126, 128, 149, 160, 174, 184, 185, 189, 265
Soxhlet, 157
Spear, 173
Spek, van der, 50, 79, 80, 81, 95
Spring, 129, 145, 172, 175, 265, 275
Stark, 171, 175
Stern, 100, 115, 174, 175
Steubing, 133, 145
Stokes, 142, 149
Svedberg, 63, 132, 143, 146, 160, 161, 162, 164, 167, 168, 173, 174, 185, 189, 274, 276
Szegvari, 145, 146

T

Tammann, 162, 168
Tanret, 218
Tendeloo, 63, 187, 189, 203, 211
Thiessen, 116, 175
Thomas, 87, 95
Thoulet, 170, 175
Titley, 275
Toth, von, 50
Traube, 49
Trivelli, 276
Tuorila, 63, 123, 128
Tyndall, 6, 7, 10, 60, 129, 130, 131, 133, 136, 172, 185, 190, 192, 198, 240, 250

V

van Arkel (see Arkel)
van Arkel-Adriani (see Arkel-Adriani)
van Bemmelen (see Bemmelen)
van Dam (see Dam)
van der Grinten (see Grinten)
van der Made (see Made)
van der Minne (see Minne)
van der Spek (see Spek)
van der Waals (see Waals)
van der Willigen (see Willigen)
van't Hoff (see Hoff)
Varga, 112, 114, 115, 116, 264
von Beckenrath (see Beckenrath)
von Dallwitz (see Dallwitz)
von Elissafoff (see Elissafoff)
von Galecki (see Galecki)
von Hahn (see Hahn)
von Helmholtz (see Helmholtz)
von Schröder (see Schroder)
von Smoluchowski (see Smoluchowski)
von Toth (see Toth)
von Weimarn (see Weimarn)
von Zawidsky (see Zawidsky)
Vorwerk, 116

W

Waals, van der, 13, 14, 49
Wächtler, 146, 251, 253
Wackenroder, 165
Walden, 95
Warburg, 50
Washburn, 204
Weaver, 160
Weigert, 145
Weimarn, von, 252, 260
Weiser, 81, 174, 276
Westgren, 121, 123, 128, 153
Whetham, 171, 172, 175
Whitney, 76, 81
Wiegner, 123, 128, 145
Wiener, 144, 160
Williams, 268, 276
Willigen, van der, 63, 87, 88, 95, 109, 111, 116, 276
Wilson, 223, 226, 249
Wintgen, 112, 113, 114, 115, 116, 188, 264
Wolff, 145, 175
Wolski, 129, 145, 174

Z

Zachmann, 49
Zawidsky, von, 49
Zeh, 88, 95
Zocher, 146
Zsigmondy, 91, 92, 95, 104, 106, 107, 109, 112, 116, 121, 125, 128, 132, 135, 141, 142, 145, 147, 148, 157, 160, 172, 173, 175, 189, 237, 241, 242, 252

SUBJECT INDEX

A

Adsorption, general discussion, 18–24
  and medium, 36, 37
  displacement, 31, 38
  interchange, 41
  isotherm, 22, 23, 27, 32, 33, 35, 36
  of electrolytes, 39–41, 44, 45, 48
  speed of adsorption, 31, 34–36
Agar-agar sol, 180, 183, 184, 192, 198–200, 216, 229, 232
  dehydrated, 194
  gelatinizing of, 232
Air bubbles, theory of, 171
Albumin, 185
Alcohol numbers, 194
Aluminium oxide sol, 165, 229, 230
Amicrons, 6
Amino-acids, dissociation of, 205–207
Arsenic trisulphide sol, 4, 5, 9, 10, 70, 71, 73, 75, 78, 79, 90, 91, 93, 108, 135, 165, 257, 273
Avogadro's constant, 141, 149, 150, 221

B

Boundary phenomena, 13–49
  liquid-gas, 13–18, 20
  liquid-liquid, 24–26
  solid-gas, 26–31
  solid-liquid, 31–41
Brownian movement, 8, 147, 148

C

Capillaries in gels, 239–243
Capillary electrical phenomena, 51–61
Capillary electrode, 51, 52
Capillary rise (or fall), 16
Cardioid condenser, 138
Carrying down of electrolytes by flocculating sols, 75–76
Casein sol, 214, 215
  protective action of, 91
  U-number action of, 92
Cataphoresis, 9, 53, 58–61, 84–86, 185, 186
  of emulsoids, 185, 186
  of gold sols, 67, 68
  of oil emulsions, 60, 68, 85
Celloidine, 251
Cellulose, 188, 234, 235
Cerium dioxide sol, 230, 250, 273
Charge, electric,
  and capillary phenomena, 51–62
  and potential, 62
  and stability, 67–75
  of emulsoids, 183–218
  of suspensoids, 11, 51–80, 82–94
Cherry gum, 251
Chromium oxide sol, 165
Classification,
  of disperse systems, 7
  of gels, 237
Cleansing action of soap, 265
Coacervation, 201–203, 235
Coagulation, see flocculation
Cobalt salts as flocculators, 75
Collodion membranes, 157, 158, 160
Colloid mill, 166
Color,
  of suspensoids, 131–133
  of the sky, 130
Condensation methods, 162–166
Critical hydration, 194
Critical potential, 68, 75, 86, 102, 194
Crystallization, velocity of, 162–164
Crystalloids vs. colloids, 8, 135, 170
Curd, 264

D
Dehydration of emulsoids,
  by alcohol, etc., 192–194
  by electrolytes, 194–197
  by tannins, 197–201
Density of sols, 179
  influence of surface tension, 16
Dialysis, 6, 9, 155–158
Diffusion, 6, 150–153, 170
Discharge,
  local —, 234
Dispergator, 166
Dispersion medium, 7
Dispersion methods, 161, 166, 167
Disperse phase, 7
Displacement adsorption, 31, 38–41
Donnan's theory, 219–223, 225
Dorn effect, 53, 62
Double layer,
  general theory, 96–111, 172, 216
  diffuse —, 98, 203
Double refracting,
  gels, 250–252
  sols, 143–145
  viscosity of —, 182
Drop method for determining particle size, 142

E
Elastic gels, 237, 243–250
Elasticity in sols, 182
Electric charge (see Charge)
Electrical disintegration, 167
Electro-dialysis, 158
Electro-endosmosis, 53–57, 82, 83
Electro-valence of double layer, 112–115
Electro-viscous effect, 183–185
Electrolyte-gelatinizing, 229, 234
Emulsifyer, 266–270
Emulsions, 265–271
  cataphoresis of, 60, 68, 85
Emulsoids, 179–227
  vs. suspensoids, 10, 11, 190, 191
External phase, 7

F
Ferric oxide sol, 9, 74, 75, 79, 87, 91, 107, 108, 143, 165, 167, 236
Filtering, 6
Flocculation, 67–80, 89–94, 105–108, 117–128
  by excessive dialysis, 87
  by several electrolytes, 271–273
  compared to gelatinizing, 229
  heat of —, 79, 169
  kinetics of —, 117–120, 122, 123
  of emulsoids, 10, 193, 194, 197, 198
  value (see limiting value)
  volume change of —, 79, 169
Flow potential, 52, 57, 58, 84
Foam, 8
Fog, 7
Formation of suspensoid sols, 161–167
Fractional flocculation, 261
Fuchsin,
  new—as flocculator, 72, 73, 90

G
Gel, 7, 229–252, 264
Gelatin,
  gel, 243, 249, 251
  in photography, 273–275
  protective action, 91, 92
  sol, 210, 212, 214–218, 224, 225
  U-number, 92
Gelatinizing, 229–236
Gold number, 91, 92
Gold sol, 67, 70, 71, 77, 91, 92, 109, 131, 132, 140–142, 154, 161, 164, 167, 216
  color of —, 131, 132
Granule, 7, 109
Gum arabic sol, 183

H
Heat of flocculation, 79, 169
HgS sol, 73, 77, 167, 272
Historical review, 169–174
Hydration,
  and electric charge, 192, 194
  and lyotropy, 196, 249, 257–259
  and reversibility, 234, 235
  as stabilizing factor, 192
  of emulsoids, 180, 181, 202, 203
Hydrolysis methods, 165
Hysteresis in gelatin sols, 217

I

Immersion ultramicroscope, 139
Internal phase, 7
Ionic micell, 264
Irregular series, 89, 90, 93
Iso-disperse, 164
Iso-electric point, 68, 206–212

L

Latent image, 274
Light,
  influence of — on colloids, 273–275
Limiting value, 10, 69–75, 125, 271–273
  and sol concentration, 78, 79
  by adding several electrolytes, 271–273
  determination of —, 69
  for arsenic trisulphide, 70, 71, 74, 75
  for dehydrated agar-agar, 193
  for ferric oxide, 74
  for gold, 70
  for mercuric sulphide, 73
Literature on colloids, 172–174
Lyophile vs. lyophobe, 10
Lyotropy, 195, 196, 249, 257–259

M

Mastic sol, 89, 130, 150–152
Maximum bubble pressure, 17
Maxwell's distribution law, 69, 127
Mechanical dispersion, 166
Membrane potentials, 225–227
Micell, 7, 109, 170
  ionic —, 264
Microns, 6
Migration potential, 53, 61
Mirror condenser, 138
MnO_2 sol, 107
Molecular dimensions,
  estimation of —, 44
Molecules,
  large — or colloidal particles, 187, 188, 190, 191, 205, 212
Molybdenum oxide sol, 258, 261
Mutarotation of gelatin sol, 217
Mutual flocculation, 91, 92

N

Nuclei,
  formation of, 162, 163

O

Oil emulsion, 68, 85
Optical phenomena,
  of gels, 231, 232, 250–252
  of sols, 5, 6, 129–145
Optically void liquids, 129
Orientation,
  of molecules, 41–49, 96–115, 208, 209, 258, 259
  of dipoles of water, 258
Osmotic phenomena,
  abnormal, 226, 227
  in general, 219–225
  of emulsoids, 223, 224
  of suspensoids, 153–155
Oxidation methods, 165

P

Paraboloid condenser, 138
Particle size,
  determination of —, 134, 140, 142, 187, 188, 223, 224
Peptization, 87, 107, 111, 112, 166, 167, 270
Photo-colloid chemistry, 273–275
Photography, 274, 275
Platinum sol, 167
Polarization,
  of fluorescent light, 129
  of Tyndall light, 129–131
Poly-disperse, 164
Potassium sol, 167
Potential of flow, 52, 57, 58, 84
Probability,
  of adhesion, 68, 69, 79, 117, 120, 125–128
  of collision, 68, 79, 117
Protective action, 91
Protein sols, 207–218
  charge of —, 186
  constitution of, 207–210
Purple of Cassius, 94

R
Radiation and colloids, 273, 274
Rapid coagulation, 121, 122
Rate,
  of coagulation, 119–128
  of crystallization, 163
  of formation of nuclei, 162
Reduction methods, 164
Reversible changes, 11, 234, 261
Röntgen rays (see X-rays)
Ruby glass, 8

S
Salting out, 194–197
Scintillation of sols, 144
Selenium sol, 121, 122, 142, 164, 272
Sensitizing of suspensoid sols, 92, 93
Silica gel, 230, 237–243
Silicic acid sol, 230
Silver halide sols, 110, 111
Silver sol, 167
Slit-ultramicroscope, 139
Slow coagulation, 123, 124
Smoke, 8
Soaps, 262–265
Sodium sol, 167
Sol, 7
Solutions,
  true and colloidal, 4, 169, 170, 173, 190, 191, 205, 207, 208
Solvation (see hydration)
Spontaneous filters, 160
Stalagmometer, 16
Star-dialyzer, 157
Starch sol, 184, 187
Stoichiometry in colloids, 5, 80, 170
  in the adsorption layer, 76, 105
  with emulsoids, 212–14
  with suspensoids, 75–77, 105, 106
Streaming potential (see flow potential)
Submicrons, 6
Sulphur sol, 93, 108, 130, 165, 166, 259–261
Surface tension, 14–17, 45
  of electrolytes, 196
  of sols, 190
  of solutions in general, 18–26
Suspensions, 8
Suspensoids, 67–174, 257–262
  vs. emulsoids, 10, 11, 190, 191
Swelling, 244–249
Syneresis, 249–250

T
Tannins, dehydration by —, 197–200
Temperature-gelatinizing, 229, 230, 232–236
Thixotropy, 236, 237, 262
Tin oxide sol, 104–107, 112–115, 165, 216
Tyndall effect, 6, 129–131, 133

U
Ultracentrifuge, 143
Ultrafilters, 158–160
Ultramicrons, 6
Ultramicroscope, 6, 135–140
  slit —, 137, 139
  immersion, 139
U-numbers, 92

V
Valence,
  influence of — on flocculation, 9, 10, 71, 171
Vanadium pentoxide sol, 143–145, 166, 251, 257, 258, 261, 262, 265
Vapor pressure,
  of small crystals, 15
  of small drops, 15, 241
  in capillaries, 241–243
Viscose, 234, 235
Viscosity, 10, 181–185
  and Poiseuille's law, 182
  of protein sols, 210, 211
  of sols of agar-agar, starch, etc., 183
Volume change on flocculation, 79, 169

W
Washing out method, 166
Water equilibrium $nH_2O = (H_2O)n$, 196
Wettability, 270, 271

X
X-rays, 133–135, 187, 188

Z
Zwitter ions, 206

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